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FORMULATION OF WATER QUALITY MODELS
FOR STREAMS, LAKES, AND RESERVOIRS:
MODELER'S PERSPECTIVE

by

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PREFACE

This report was published under the Water Quality Research Program (WQRP), which is sponsored by the Headquarters, US Army Corps of Engineers (HQUSACE), and is assigned to the US Army Engineer Waterways Experiment Station (WES), under the purview of the Environmental Laboratory (EL). The WQRP is managed under the Environmental Resources Research and Assistance Programs (ERRAP). The HQUSACE Technical Monitor of WQRP is Mr. David P. Buelow. Mr. J. Lewis Decell, WES, is the Program Manager of ERRAP.

This report was originally written as a paper for the International Symposium on Water Quality Modeling of Agricultural Non-Point Sources, which was held at Utah State University, Logan, UT, on 19-23 June 1988. The paper was published as this report to make the information more available to Corps of Engineers offices and others. The authors are Dr. Heinz G. Stefan, Department of Civil and Mineral Engineering, St. Anthony Falls Hydraulic Laboratory, University of Minnesota, Minneapolis, MN; Mr. Robert B. Ambrose, Jr., Environmental Research Laboratory, US Environmental Protection Agency, Athens, GA; and Mr. Mark S. Dortch, Chief, Water Quality Modeling Group, Ecosystem Research and Simulation Division, EL, WES. This report was edited by Ms. Lee T. Byrne of the WES Information Technology Laboratory.

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FORMULATION OF WATER QUALITY MODELS FOR STREAMS, LAKES, AND
RESERVOIRS: MODELER'S PERSPECTIVE

PART I: CONCEPTS OF SURFACE WATER QUALITY MODELING

Categories

1. Surface water quality (WQ) models can be categorized in various ways. One is with reference to their formulation. On that basis, models may be classified by the following distinctions:

- a. Physical versus mathematical/numerical.
- b. Mechanistic versus empirical.
- c. Deterministic versus stochastic.
- d. Steady-state versus unsteady.
- e. Dimensionality (0, one-dimensional (1-D), two-dimensional (2-D), and three dimensional (3-D)).
- f. Hydrodynamic assumptions.
- g. Biogeochemical formulations.

This paper deals with only mathematical/numerical, mechanistic, deterministic surface WQ models. Compilations of available operational surface water models including those that deal with water quality have been given at various times by various organizations in the United States, e.g. by (a) Hydrologic Engineering Center, US Army Corps of Engineers, Davis, CA (1987); (b) US Geological Survey (USGS) (Jennings and Yotsokura 1980); (c) Office of Technology Assessment, US Congress (1982); (d) US Environmental Protection Agency (USEPA), Center for Water Quality Modeling (1980), Athens, GA; and (e) US Army Engineer Waterways Experiment Station, Vicksburg, MS (1987).

2. The state of toxicant modeling in surface water was reviewed in 1979 (USEPA 1980); Figure 1 shows an example of the systems used. There have been no substantive changes in the concept and/or dimensionality of the models, but the number of recognized pollutant materials and interacting transformations has increased dramatically.

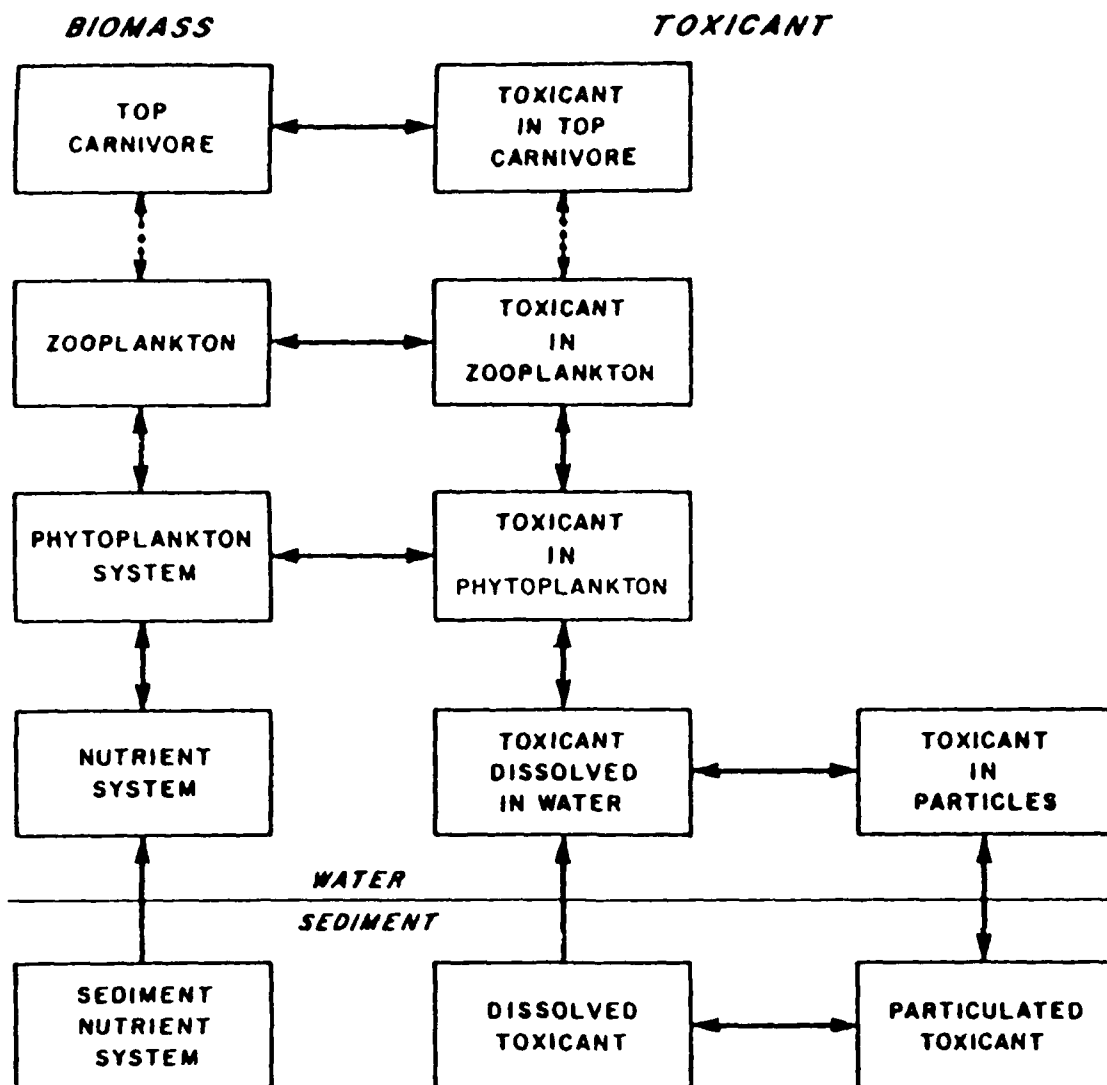


Figure 1. Systems in toxicant WQ models (from USEPA (1980))

Approach

3. The classical approach to mechanistic model formulation is to subdivide each water body into a suitable number of control volumes. "Suitable" depends on the purpose of the modeling effort, the shape and size of the water body, and especially the time scale (years, months, weeks, days, or even hours) to be modeled. The time scale influences the choice of physical transport and chemical and biological transformation processes to be included in the model. This selection process is presently more an art than a science.

One rule of thumb is that the shorter the time scale and the larger and more complicated the geometry, the more control volumes will be required. Another rule is to select the longest possible time scale because averaging over long times often makes the model easier. Science takes over when the basic equations for each control volume are formulated. These equations are transport (conservation) equations for mass of water and transport/transformation equations for materials in the water. The latter may include expressions for energy transfer and expressions for chemical equilibrium or chemical and biological kinetics. Water quality parameters that have been modeled include:

- a. Total dissolved solids (TDS), inorganic salts.
- b. Inorganic suspended sediments (SS).
- c. Temperature (T).
- d. Organic wastes and dissolved oxygen (DO) (biochemical oxygen demand (BOD)).
- e. Bacteria (Ecoli).
- f. Nutrients (phosphorus, nitrogen, silicon).
- g. Inorganic carbon (carbon (C), pH).
- h. Biomass and food chains (chlorophyll *a* (Chl *a*), C, zooplankton, etc.).
- i. Metals (lead, mercury, cadmium).
- j. Synthetic organic chemicals (polychlorinated biphenyls (PCBs)).
- k. Radioactive materials (radium, plutonium).
- l. Herbicides, insecticides (Dieldrin, dichlorodiphenyltrichloroethane (DDT)).

The classical formulations for nutrient uptake, growth (including photosynthesis), predation, and microbial decomposition are widely used. Recent needs are for models of toxic materials in the form of metals such as mercury, lead, and cadmium; organics such as PCBs; herbicides; and insecticides and for models simulating lowered pH values caused by acid rain.

4. Since it is possible to produce a nearly infinite number of equations, the question to be answered by the modeler is not "how many equations can I write" but "how many need to be written to solve the problem at hand." The ideal model is the one with the smallest number of equations that can solve the problem.

5. All models are formulated for a particular purpose. There is no all-purpose model, and it is unlikely that one will ever be developed. Some

models may serve several purposes. It was the consensus of the participants in a 1979 USEPA workshop (USEPA 1980, Thomann 1982) that the formulation of a surface WQ model requires the interaction of three types of people:

(a) managers who recognize a WQ problem, (b) specialists who understand or are capable of studying the processes which relate to the problems at hand, and (c) modelers who can synthesize all information pertaining to the problem in mathematical form and solve the resulting mathematical relationships. Only in very simple cases may one person be able to fulfill all three roles.

6. General steps by which a surface WQ model is developed and put to use are:

- a. Specification of problems, issues, and objectives.
- b. Specification of theoretical concepts and mathematical relationships (model selection).
- c. Quantitative specifications of parameters/coefficients and boundary conditions.
- d. Model calibration.
- e. Model verification.
- f. Determination of model sensitivity, accuracy, and uncertainty.
- g. Application.

To this list, a No. 8 postapplication model audit should be added (Thomann and Mueller 1987).

7. Conferences on WQ modeling have dealt with eutrophication (Federal Water Pollution Control Administration (FWPCA) 1969, Lorenzen 1981), DeGray Lake (Kennedy and Nix 1987), general issues (Ott 1976, Nix and Black 1987), toxic substances (Jorgensen 1984), and ecological modeling (Jorgensen 1979a).

8. Parameter values for WQ models must often be developed through field and laboratory studies. Initial estimates may be found in handbooks (e.g. Jorgensen 1979b). Data sets that can be used for model calibration and verification are usually assembled on a case-by-case basis. A compilation for four rivers, two lakes, and one estuary was given by Huber, MacIntyre, and Heavey (1984).

9. In the following sections, some concepts and accomplishments of WQ modeling are presented. Specifically the following are addressed:

(a) hydrodynamic transport in standing and flowing waters, (b) suspended sediment transport modeling and sediment/WQ interactions, (c) modeling of organic wastes nutrients and eutrophication, and (d) modeling of toxic material

transport and transformation including synthetic organics (pesticides, insecticides) and metals. The report concludes with a list of some challenges for the future as perceived by the authors.

PART II: WATER QUALITY MODELS FOR STANDING WATERS
(RESERVOIRS, PONDS, AND LAKES)

Approaches

10. The features and characteristics of reservoir, lake, or pond WQ models are directly related to the peculiar thermo-hydrodynamics in such water bodies, which make them substantially different from streams and rivers. In rivers and streams, gravity is the main driving force, and bed friction is the main resisting force, resulting in usually very perceptible velocities and strong tendency to turbulent mixing. Lakes, ponds, and reservoirs are often characterized by water movements that are very slow and weak. The driving forces are from wind shear, solar radiation, heat exchange, and inflows and outflows. Very small density differences caused by temperature gradients from surface heating/cooling and/or by gradients in dissolved or suspended substances (salinity gradients, turbidity) often control the thermo-hydrodynamics of standing waters. Phenomena that are usually absent or can be ignored in river and stream flow analysis are dominant in "standing" waters, e.g., stable temperature stratification that hinders vertical turbulent mixing; natural convection caused by unstable density stratification; wind-driven circulation and vertical mixing; density and turbidity currents; and selective withdrawal from density-stratified water. The reader can find overviews of the hydrodynamic features of lakes, reservoirs, impoundments, and ponds in summaries by Mortimer (1974), Wetzel (1975), Gibbs and Shaw (1977), Lerman (1978), Graf and Mortimer (1979), Imberger (1979), Csanady (1980), Stefan (1981), Harleman (1982), Imberger and Hamblin (1982), Henderson-Sellers (1984), Shanahan and Harleman (1984), and Annandale (1987).

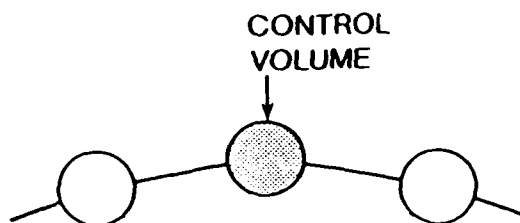
11. Hydrodynamics are the basis for many significant differences in ecosystems of lakes/reservoirs and rivers/streams. Lakes that often have the longest residence times of water (defined here as total volume of lake divided by total outflow) develop seasonal successions of organisms and chemical processes not affected by the swift motion found in rivers and streams. Storage reservoirs can differ from lakes because of the dominant effects of water level fluctuations and inflow. River impoundments created to make waterways navigable may have fairly constant water levels but highly variable residence

time making them "typical" lakes at low flows and "typical" rivers at high flows.

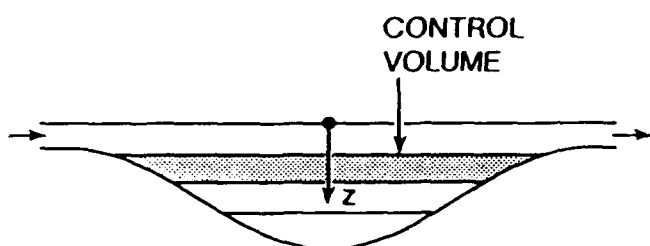
12. The interactions with the bed also are very different in flowing and standing waters. Slow deposition of fine and organic material on lake/reservoir beds can have a significant effect on water quality. Equally important can be the release of materials (remineralized substances) from the bed due to chemical processes or bacterial decomposition. Bioturbation by invertebrates, fishes, etc., or wind-driven resuspension can contribute greatly to WQ deterioration. In rivers the contributions of such processes are often negligible compared with advective transport of water quality.

13. Water quality models of lakes, reservoirs, ponds and impoundments can be formulated as zero-, one-, two- or three-dimensional (0-D, 1-D, 2-D, or 3-D) in space (Figure 2). A 0-D model will average concentration over the entire water body without allowing variation in space; it will use only one control volume for the entire lake or pond. A 1-D model for standing water usually includes the vertical dimension to account for stratification; thus the model uses a series of horizontal layers. The 2-D models for standing waters are either longitudinal-vertical for density stratified waters or depth integrated in nonstratified, shallow waters of large horizontal dimensions. In longitudinal-vertical coordinate systems, concentrations are given as $C(x,z)$ where x can be a longitudinal coordinate of a reservoir and z a depth coordinate. Variations in concentration across the width are not treated in such a model, and concentrations are assumed averaged with width y . Such a model will require the use of control volumes stacked with depth and length.

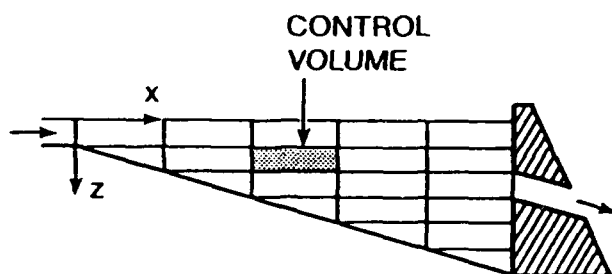
14. Selection of the lowest possible dimensionality, i.e. the smallest number of control volumes (CV) is the most advantageous since a conservation equation must be written for each CV and each WQ constituent. Selection of the dimensionality of a lake, reservoir, pond, or impoundment WQ model may be thought to depend mostly on the size of the water body, but it has been shown to be really a function of the purpose of the model. The North American Great Lakes, for example, have been modeled very successfully as completely mixed 0-D continuous flow reactors to develop phosphorous management strategies for eutrophication control (Chapra 1977, Chapra and Reckhow 1983). Lake/reservoir WQ models of different dimensionalities are discussed in the following sections.



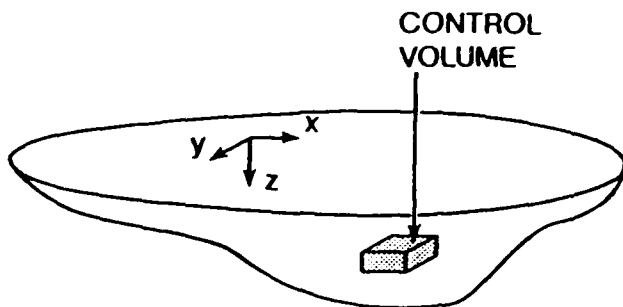
0-D $C(t)$
MIXED CELL



1-D $C(z,t)$
STRATIFIED LAKE



2-D $C(x,z,t)$
STRATIFIED RESERVOIR
WITH VERTICAL AND
HORIZONTAL GRADIENTS



3-D $C(x,y,z,t)$
THREE-DIMENSIONAL LAKE

Figure 2. Dimensionality of lake/reservoir models

Zero-Dimensional Models of Reservoirs, Ponds, and Lakes

15. Zero-dimensional (0-D) WQ models of lakes, reservoirs, and ponds contain no information on hydrodynamics other than the hypothesis that the water body is well mixed. They are also referred to as input-output models, box models and alike. The input I of a material (nutrient, toxic, etc.) in units of kilograms per cubic metre per year ($\text{kg m}^{-3} \text{yr}^{-1}$) and the concentration $C(t)$ of the material in units of kg m^{-3} in the well-mixed water body are then related by the conservation equation

$$\frac{dC}{dt} = I - \frac{C}{\theta} \quad (1)$$

This equation can be solved for various loading functions $I(t)$ and an initial condition $C = C(0)$; t = time; I = the sum of material inflows (a) from all possible sources in the watershed through tributaries, drains, sewers, and overland flow, (b) from the atmosphere, (c) from ground water, and (d) from internal sources, e.g. the sediments. The input I is related to the loading L in kg yr^{-1} and the lake volume V in m^3 by $I = L/V$. A distinction between nonpoint sources and point sources is common.

16. The parameter θ is a time constant in units yr^{-1} . It sums the rate coefficients of all first-order processes by which the material is removed from the water, e.g. by an outflow Q_0/V or by a settling process $V_s A C/V$ or by a chemical transformation (reaction) at rate $K_1 C$ or by a biological transformation (e.g. bacterial decomposition or zooplankton grazing) at rate $K_2 C$, all in units of $\text{kg m}^{-3} \text{yr}^{-1}$. Q_0 is a volumetric outflow rate in $\text{m}^3 \text{yr}^{-1}$, V_s is a bulk "settling loss" velocity in m yr^{-1} , and A is the surface area of a lake in m^2 . The rate coefficients Q_0/V for outflow, AV_s/V for settling loss, K_1 for chemical, and K_2 for biological transformations are related to the time constant θ in Equation 1 by

$$\frac{1}{\theta} = \frac{Q_0}{V} + \frac{AV_s}{V} + K_1 + K_2 \quad (2)$$

If other first-order processes are important, Equation 2 can be expanded to

include them. It is evident from Equation 2 that different residence times exist for different compounds (materials) and lakes/reservoirs.

17. Equations 1 and 2 can be used to quantify not only existing conditions in a lake or reservoir, but also to explore the effects of various alternative management and restoration techniques. For example, a flushing technique can be represented by an increase in Q_0 ; a reduction in pollutant load by watershed management techniques, diversion, pretreatment, and sediment sealing can be represented by smaller values of I ; dredging or water-level rise can be represented by an increase in V and in-lake treatment, e.g. by flocculation or chemical treatment; or some form of biomanipulation can be represented by increased values of V_s , K_1 and K_2 , respectively.

18. Zero-dimensional models have proven to be very useful and cost-effective for evaluation of long-term effects, measured usually in years. An early, spectacular application was to the restoration of Lake Washington; subsequently many other applications to single lakes were made (e.g. Middlebrooks et al. 1974, Sonzogni et al. 1976,). Failure to recognize important processes in 0-D models, e.g. of material release from the sediments, has led to mispredictions, e.g. of P in eutrophic lakes.

19. The very well-known Vollenweider and Dillon and Rigler models for eutrophication control in lakes by P management are extensions of the 0-D models and can be obtained by mainly adding empirical relationships between P and chlorophyll a (Chl a) as a measure of biomass concentration, as shown by Chapra and Tarapchak (1976).

20. Zero-dimensional models can also be used to simulate series of lakes or lake networks by using the output $C(t)$ of the most upstream lake as input to the following one, etc. An application to the Great Lakes was given by Chapra (1977). It was used to evaluate and predict the effectiveness of several phosphorous management alternatives including P-ban in detergents, P-removal from municipal sewage by tertiary treatment, changes in agricultural practices, etc. A summary of the model and its application is given in Chapra and Reckhow (1983).

21. The idea has been further extended also to interconnected bays and channel systems such as found in coastal plains or in shallow impoundments (Stefan and Anderson 1980, Demetracopoulos and Stefan 1983). In that case, gravity and wind-driven circulation could be simulated on a daily or even hourly time scale. Shortening the time scale is essential when flows are

highly time variable in response to weather. A model applicable to tidal situations was developed by Schaffranek, Baltzer, and Goldberg (1981). Zero-dimensional models are also applied to bays connected to larger water bodies (Chapra 1979). In that case the exchange flow rates (in and out) across the mouth of the bay must be specified based on either tracer observations or hydrodynamic analysis. Exchange across the mouth of the embayment can be larger than inflow.

One-Dimensional Models of Reservoirs, Ponds, and Lakes

22. If water quality variations are to be predicted throughout a season, i.e. on a monthly, weekly, or even daily scale, internal hydraulics of a lake or reservoir cannot be ignored. Temperature stratification occurs in most "standing waters" in temperate regions, and the associated density stabilities cause vertical gradients in water quality during the summer and winter seasons. One-dimensional WQ models that describe water temperature and concentrations $C(z,t)$ as a function of depth and time are therefore needed (Figure 3). In such models the lake or reservoir is described by a system of horizontal layers each of which is well mixed. Vertical transport of heat or material compounds between layers is described by a diffusion equation in which a bulk vertical turbulent diffusion coefficient $K_z(z)$ is incorporated in a heat conservation equation of the form

$$A \frac{\partial T}{\partial t} = \frac{\partial}{\partial z} \left(K_z A \frac{\partial T}{\partial z} \right) + \frac{H}{\rho c} \quad (3)$$

where

$A(z)$ = horizontal area of the lake as a function of depth

$T(z,t)$ = water temperature as a function of depth z and time

$H(z,t)$ = internal distribution of heat sources due to radiation absorption inside the water column

23. At the water surface, heat fluxes caused by solar radiation, atmospheric radiation, back radiation, evaporation, and convection are applied. The expressions used for these fluxes cannot be presented here but can be found in Edinger, Duttweiler, and Geyer (1968); Edinger, Brady, and

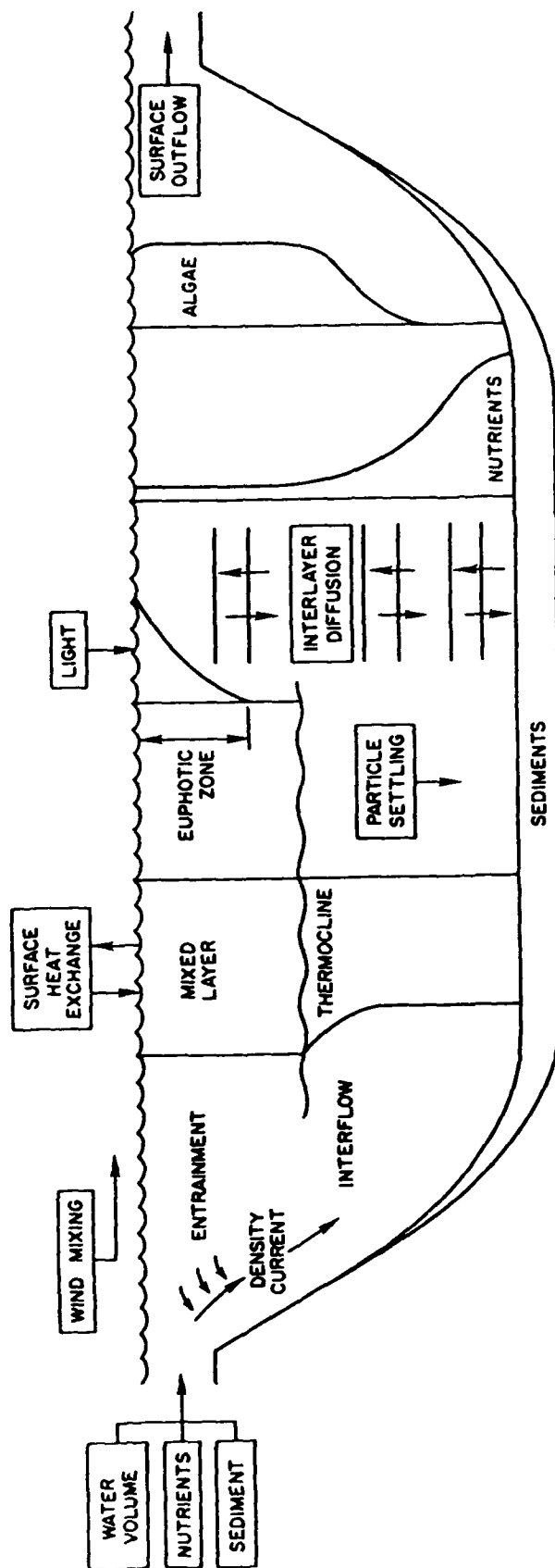


Figure 3. Schematic representation of the variables and processes simulated in the 1-D MINLAKE model

Geyer (1974); Ryan, Harleman, and Stolzenbach (1974); Stefan and Gulliver (1980); and Harleman (1982).

24. There are basically two methods that have been used for computing total net heat transfer at the water surface. In the first method, each of the fluxes is computed and added to form the total net surface heat transfer, which is then converted to a rate of temperature change for use in the temperature balance equation. Several of the flux terms are dependent on the water temperature; thus, the most recently computed value in the model for the water temperature is used in computing these terms. This approach is referred to as a direct energy balance.

25. The alternative approach is based on the equilibrium temperature concept, which states that when the water temperature equals the equilibrium temperature, heat exchange does not occur (Edinger, Duttweiler, and Geyer 1968). With the water temperature set equal to the equilibrium temperature and with the total net heat transfer set to zero, the flux terms can be expressed in terms of the equilibrium temperature (Edinger, Brady, and Geyer 1974); the equilibrium temperature can then be solved iteratively and independently of the thermal simulation. The total net heat transfer becomes the difference in the equilibrium temperature and water temperature times a heat transfer coefficient that can also be computed prior to the temperature simulation.

26. Both approaches for heat transfer require project location (latitude, longitude, and altitude) and meteorological data (dry bulb temperature, wet bulb or dew point temperature, wind speed, cloud cover, and atmospheric pressure).

27. The internal source $H(z,t)$ is generated by solar radiation that penetrates into the water. The amount of solar radiation absorbed in each layer is approximated by Harleman (1982) as

$$H(z,t) = (1 - \beta)(1 - r)\phi_s \frac{\partial}{\partial z} \left[A e^{-\eta(z_s - z)} \right] \quad (4)$$

where

β = surface absorption (~40 percent)

r = reflectivity

ϕ_s = solar radiation = $\phi_s(t)$

η = attenuation coefficient

z_s = elevation of water surface

28. In reservoirs that have inflows and outflows, Equation 3 must be expanded (Huber, Harleman, and Ryan 1972; Orlob and Selna 1970).

$$A \left(\frac{\partial T}{\partial t} \right) + \left[\frac{\partial (Q_v T)}{\partial z} \right] = \frac{\partial}{\partial z} \left(K_z A \frac{\partial T}{\partial z} \right) + (B u_i T_i) - (B u_o T) + \frac{H}{\rho c} \quad (5)$$

where

Q_v = vertical flow rate

u_i and u_o = horizontal inflow and outflow velocities

T_i = inflow temperature

B = reservoir width at depth

To satisfy continuity, Q_v must satisfy

$$Q_v(z, t) = B \int_0^z (u_i - u_o) dz \quad (6)$$

In a 1-D approach, determination of $q_i(z) = B(z)u_i(z)$ may require analysis of density currents through multilayered systems, such as shown by Akiyama and Stefan (1984, 1987). Determination of outflow may require analysis of stratified (selective) withdrawal such as described by Brooks and Koh (1969) and Huber, Harleman, and Ryan (1972).

29. If the numerical solution of Equations 4 and 5 is done with fixed vertical coordinates such as described by Orlob and Selna (1970) for one of the earliest reservoir models, the computations with a moving free surface become cumbersome. A more recently introduced alternative of a Lagrangian nature keeps track of reservoir volumes in a stack of expandable/contractible layers and determines the position of those layers by comparing cumulative volume curves for layers to the topography-dependent lake-specific volume characteristic $V(z)$. This is used in models DYRESM (Imberger and Hamblin 1982), RESQUAL II (Stefan, Cardoni, and Fu 1982) and CE-QUAL-R1 (Environmental Laboratory 1986a).

30. The vertical turbulent diffusion coefficient is usually introduced as an empirical function $K_z(\epsilon)$ of a density stability parameter ϵ or N^2 ,

where

$$\epsilon = \frac{1}{\rho} \frac{d\rho}{dz} \text{ and } N^2 = \epsilon g \quad (7)$$

Uncertainty in the K_z values is often large. Attempts to relate K_z not only to stability which hinders the development of vertical turbulence, but also to the forcing elements, particularly wind, and inflows have been only partially successful. A recent review of this subject has been given by Ford and Johnson (1986). From stability and boundary layer theory, McCormick and Scavia (1981) derived the expression:

$$K_z = \frac{u_*^3}{\beta g \alpha \left(\frac{\partial T}{\partial z} \right) k^2 z^2} \quad (8)$$

where

u_* = wind-induced surface shear velocity = $\sqrt{\tau_w / \rho}$

β = empirical coefficient = 3.5×10^{-4} for Lake Ontario

g = acceleration of gravity

α = coefficient of thermal expansion

k = von Karman constant ~ 0.4

z = depth below surface

τ_w = wind-induced surface shear stress $\sim 0.0015 \rho_a W^2$

ρ_a = air density

W = wind velocity

When thermal instability sets in, natural convection usually produces complete mixing over the range of instability plus a region of penetrative mixing. This high rate of mixing is usually well handled by very high values of $K_z(z)$. An alternative to turbulent vertical diffusion coefficients is the use of k - ϵ closure models (Rodi 1980). This approach was used to give 1-D vertical temperature distributions in Lake Vanern, Sweden (Omstedt 1984). An expression of the following form can be used (Stefan and Ford 1975) to predict mixed layer depth h :

$$\frac{1}{2} \frac{dh}{dt} \frac{\Delta \rho g h}{\rho_o u_*^3} \approx \text{Constant} \quad (9)$$

where

$\Delta \rho$ = density differential between mixed layer and next adjacent layer below

u_* = shear velocity due to wind during time interval dt

When the stratification is strong, dissipation becomes important. Therefore Equation 9 was extended by Bloss and Harleman (1979).

31. The transport and transformation of dissolved substances in a 1-D vertically stratified WQ model are described by an equation similar to Equation 5.

$$V \frac{\partial C}{\partial t} = -Q_z \frac{\partial C}{\partial z} \Delta z + \frac{\partial}{\partial z} \left(K_z A \frac{\partial C}{\partial z} \right) \Delta z + Q_i C_i - Q_o C \pm S \quad (10)$$

Equations 5 and 10 are equivalent and are given by Orlob and Selna (1970) and Huber, Harleman, and Ryan (1972), respectively. The sink/source term S includes chemical and biological transformations and can take many different forms. One of the simplest is a single first-order reaction. $S = K_1 C V$, where K_1 is a rate coefficient. For suspended materials, a settling term $- [\partial(V_s C A) / \partial z] \times \Delta z$ must be added to the right-hand side of the equation, where V_s = settling velocity of the particles.

32. There exist a large number of 1-D WQ models of the kind described. A survey was given by Orlob (1983). The authors are acquainted with Orlob and Selna's model (1970); Huber, Harleman, and Ryan's model (1972); Stefan, Cardoni, and Fu's RESQUAL II (1982); Imberger and Patterson's DYRESM model (Fischer 1981); the Hydrologic Engineering Center HEC-5 models (1986); CE-QUAL-R1 (Environmental Laboratory (1986a); and Riley and Stefan's MINLAKE model (1987). Other similar 1-D reservoir models are the Tennessee Valley Authority's (TVA's) WRMMS (TVA 1976) and RESTEMP (Brown and Shiao 1981) models; and a USGS model (House 1981). All of these basically 1-D hydrodynamic models simulate temperature stratification, but CE-QUAL-R1 and MINLAKE also handle a large array of WQ parameters such as dissolved oxygen, algae, nutrients, and conservative substances. CE-QUAL-R1 is designed for reservoirs; MINLAKE is intended for lakes. A similar model FARMPOUND for small

rural impoundments was developed by the US Department of Agriculture/ Agricultural Research Service.

33. The CE's vertically 1-D model CE-QUAL-R1 (Environmental Laboratory 1986a) simulates temperature plus as many as 34 other WQ parameters. Primary physical processes included are surface heat transfer, shortwave and longwave radiation and penetration, convective mixing, wind- and flow-induced mixing, entrainment of ambient water by pumped-storage inflows, inflow density current placement, selective withdrawal, and density stratification as impacted by temperature and dissolved and suspended solids. Major chemical and biological processes in CE-QUAL-R1 include: the effects on DO of atmospheric exchange, photosynthesis, respiration, organic matter decomposition, nitrification, and chemical oxidation of reduced substances; uptake, excretion, and regeneration of phosphorus and nitrogen and nitrification-denitrification under aerobic and anaerobic conditions; carbon cycling and alkalinity-pH-CO₂ interactions; trophic relationships for phytoplankton and macrophytes; transfers through higher trophic levels (i.e. zooplankton and fish); accumulation and decomposition of detritus and organic sediment; coliform bacteria mortality; and accumulation and reoxidation of manganese, iron, and sulfide when anaerobic conditions prevail.

34. The US Army Engineer Waterways Experiment Station (WES) has expended considerable effort during the past 20 years to develop a single generalized model for prediction of outflow water quality at dams, building on the work of Brooks and Koh (1969) and many others. Smith et al. (1987) synthesized the various point sink models into a single generalized, point sink model. The WES's selective withdrawal models have been coded into a documented program referred to as SELECT (Davis et al. 1987). When used as a stand-alone program, SELECT computes the in-pool vertical distribution of outflow and outflow concentrations of WQ constituents, given the in-pool vertical distribution of water density and WQ constituent concentrations, the outlet configuration and depth, and the discharge rate. In subroutine form, SELECT is used in reservoir WQ models, e.g. CE-QUAL-R1 (Environmental Laboratory 1986a), to compute the outflow distribution and release water quality. Numerical hydrodynamic models for stratified flow, such as the WESSEL (Thompson and Bernard 1985) and STREMR (Bernard, in preparation) codes, can be used as experimental tools to study the withdrawal characteristics of unusual outlet configurations.

Two-Dimensional Models of Reservoirs, Ponds, and Lakes

35. Two-dimensional (2-D) WQ models were developed for long, deep reservoirs in which significant vertical WQ gradients are coupled with horizontal ones. For example, Lake Powell and Lake Mead reservoirs on the Colorado River require such an approach. A few 2-D models are available. One is the Laterally Averaged Reservoir Model (LARM) model developed by Edinger and Buchak (1983) and Buchak and Edinger (1984a, 1984b); another is the Computation of Reservoir Stratification (COORS) model by Waldrop, Ungate, and Harper (1980); Harper and Waldrop (1980a, 1980b); and TVA (1986). Both models solve advection/diffusion equations in a vertical-longitudinal plane through a reservoir. The models are width integrated. These models can predict the 2-D temperature structure of deep reservoirs throughout the annual stratification cycle and compute temporal and spatial hydrodynamics of reservoirs to provide advective components for WQ models. A later version of LARM, referred to as CE-QUAL-W2 (Environmental Laboratory 1986b), has been modified by the CE to include 20 WQ constituents.

36. Temperatures and velocity gradients of deep storage reservoirs occur primarily in the longitudinal (x) and vertical (z) directions. However, lateral (y) contributions of shear stress, continuity, etc., are important, but their effects can be included through an integration procedure in the lateral direction. This procedure reduces by one the number of equations and independent variables by eliminating the y-momentum equation and simplifying the remaining equations. Additionally, most vertically stratified hydrodynamic/transport models for reservoirs (and other surface waters) make the hydrostatic assumption, which reduces the vertical equation to a simple pressure gradient relation.

37. Empirical functions are defined to include the effects of turbulent processes that occur at a scale smaller than the resolution afforded by the solution procedure (i.e., a finite difference grid). The technique chosen in the COORS model is to assume that the effects of turbulence could be incorporated by using Prandtl's mixing length hypothesis where the mixing length is defined by half the vertical spacing between grid planes.

38. Boundary conditions included in most 2-D models are inflows and outflows (flow rate and temperature must be specified for inflows), bedshear, no heat transfer through the bed, heat flux through the free surface, and

surface wind shear. These conditions are similar to those imposed in the 1-D models.

39. The numerical solution of the equations in the COORS model is explicit and time marching, whereas the water surface solution of the CE-QUAL-W2 model is implicit, so that larger time-steps can be taken. Finite differences are used to discretize the equations in both models.

40. CE-QUAL-W2 consists of directly coupled hydrodynamic and WQ transport models. Hydrodynamic computations are influenced by variable water density caused by temperature, salinity, and dissolved and suspended solids. Developed for reservoirs and narrow, stratified estuaries, CE-QUAL-W2 can handle a branched and/or looped system with flow and/or head boundary conditions. With two dimensions depicted, point and nonpoint loadings can be spatially distributed. Relative to other 2-D models, CE-QUAL-W2 is efficient and cost-effective to use.

41. In addition to temperature, CE-QUAL-W2 simulates as many as 20 other WQ variables. The physical, chemical, biological processes of CE-QUAL-W2 are very similar to those in CE-QUAL-R1 with the following exceptions: it does not include transfer to higher trophic levels of zooplankton and fish; it does not account for substances that are accumulated in the sediments other than organic matter; it contains only one algal group rather than three; it does not include macrophytes; and it does not include the sediment release and oxidation of sulfur and manganese when anaerobic conditions prevail, although it does allow specification (as a boundary condition) of flux from the sediments of iron, ammonia nitrogen, and phosphate phosphorus during anaerobic conditions.

42. A box model approach to 2-D reservoir modeling was used by Brown (1985). The model, named BETTER for Box Exchange Transport Temperature and Ecology of Reservoirs, has been applied to TVA reservoirs. In this model, the reservoir is segmented into an array of volume elements or boxes. These boxes are described with a volume, an upper interface or surface area, and a downstream conveyance area. The BETTER model uses a floating layer scheme, so that the layer boundaries remain at specified depths relative to the surface elevation. The layer spacing is arbitrary and can be changed by the user if vertical gradients are not being adequately reproduced.

43. In the BETTER model, the flow patterns in the lake or reservoir are modeled as longitudinal and vertical flow transfers between the array of

volume elements. Daily flow patterns can be calculated based on the inflow and outflow. The flow patterns are influenced by the temperature patterns. The inflow temperature governs where the inflow will enter the water column, and subsequent flows will move through the reservoir along matched density pathways. In addition to horizontal and vertical flows (transport), vertical mixing (exchange) can be simulated. Mixing may be caused by wind surface cooling or turbulent flows. Volumetric exchanges between adjacent layers or a diffusive formulation can simulate mixing. A surface mixed layer can be calculated for each day in response to surface cooling and wind mixing.

44. An introduction to box-type multidimensional model was given by Chen and Smith (1979) and a review by Shanahan and Harleman (1984). A 2-D box-type model for water quality has also been used for Lake Erie (Lam, Schertzer, and Fraser 1983).

45. The most recent development in 2-D reservoir modeling include (a) the replacement of eddy diffusion coefficients and mixing length theories by other turbulence closures, e.g. $k-\epsilon$ models, and (b) the solution of the fundamental, fully convective primitive equations on powerful supercomputers. Examples of this approach have been given by Ni et al. (1985), Thompson and Bernard (1985), Farrell and Stefan (1986), and Sauvaget (1987). At this stage of development, these models are pure hydrodynamic models. Water temperature (or water density) is the only WQ parameter used.

46. Selection of a width-integrated x,z -coordinate system in a vertical plane is appropriate for 2-D models of long and deep reservoirs. Depth-integrated models using x,y -coordinates are appropriate for shallow and wide lakes. Bennett, Clites, and Schwab (1983) described a typical 2-D lake circulation model. These models are typically driven by wind shear and include no stratification effects on vertical turbulence since they are depth integrated. This approach was used to model Lake Balaton in Hungary (van Straten and Somlyódy 1980). Other examples are given by Shanahan and Harleman (1984).

Three-Dimensional Models of Reservoirs, Ponds, and Lakes

47. Three-dimensional (3-D) WQ models have not been used extensively because of the computational expense, as well as for other reasons. Lake and reservoir 3-D flow simulations have been made by Simons (1973, 1975, 1976) and Leendertse and Liu (1975) and verified in both small and large lakes. A

special version was produced by Kielmann and used for pollutant transport in the Baltic Sea (Funkquist and Gidhagen 1984). The model uses seasonally and depth-varied (six layers) eddy viscosities and eddy diffusivities. These models do not overcome the uncertainty in the turbulence closing, but the predicted circulation is a reasonable synthesis of wind-induced and thermocline circulation. The diffusive transport created by turbulence smaller than the grid size in the horizontal (several kilometres) is modeled by a Monte Carlo technique. This means that the calculated turbulent part of the particle velocity is related to the eddy diffusivity in a physically correct way. Some results obtained for the North American Great Lakes have been used in a 3-D WQ model for Lake Ontario (Thomann et al. 1975; Thomann, Winfield, and Segna 1979). The WQ models are of the multiple-box type, i.e. multilayered in the vertical and each layer subdivided into very large elements representative of the coastal regions and the pelagic waters (Figure 5). Advective and dispersive flows between boxes are determined by flow budgets based on long-term observed hydrology. Relying on the National Oceanic and Atmospheric Administration Geophysical Fluid Dynamics Laboratory, researchers at Princeton and Stevens Institute of Technology are compiling a massive 3-D time-dependent model of the New York-New Jersey estuary. A similar effort is being conducted by the WES for studying eutrophication problems in Chesapeake Bay.

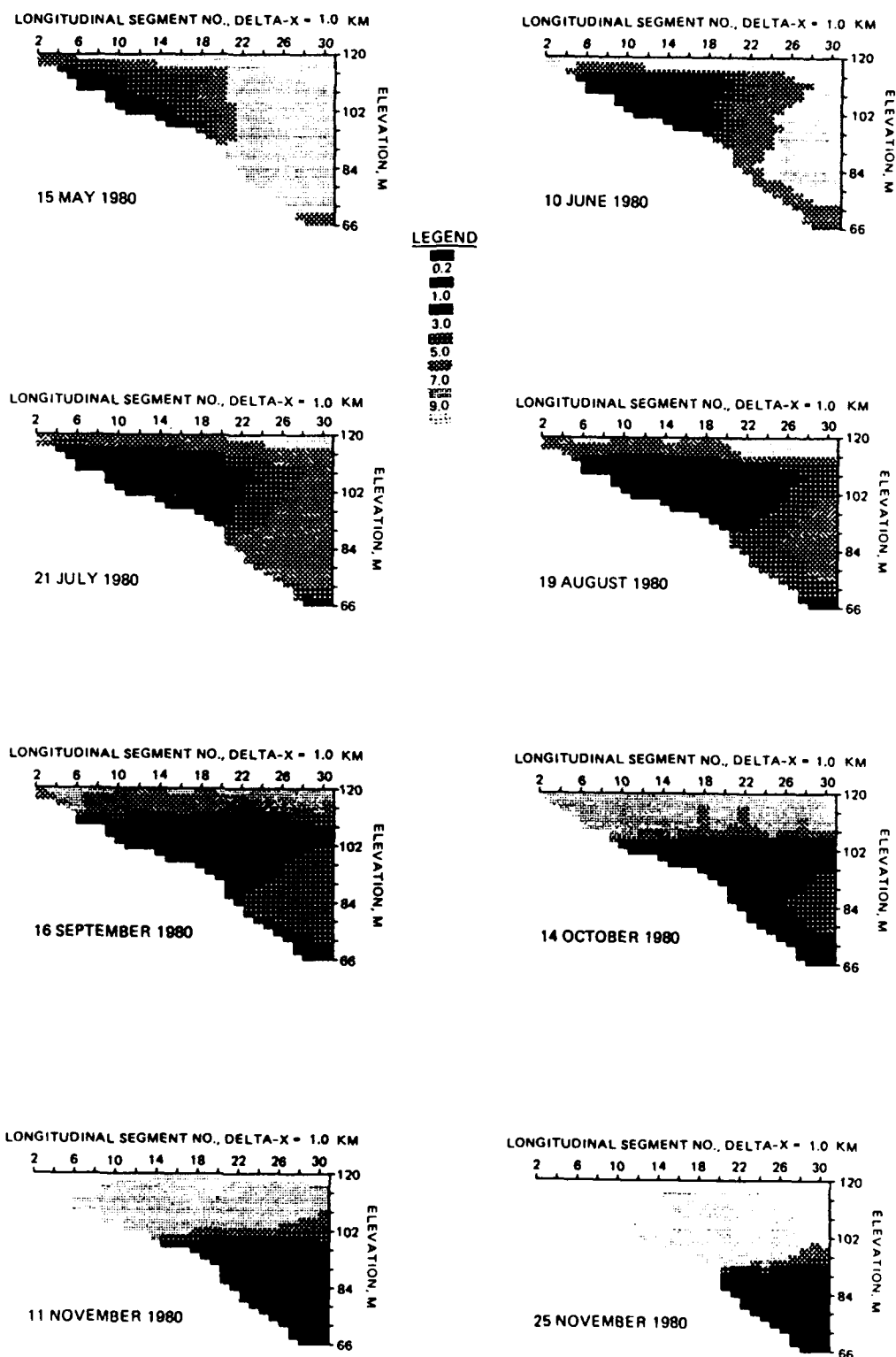


Figure 4. Shaded contours of predicted DO concentration using CE-QUAL-W2 (Martin 1987) DeGray Lake verification simulations (concentrations milligrams per litre)

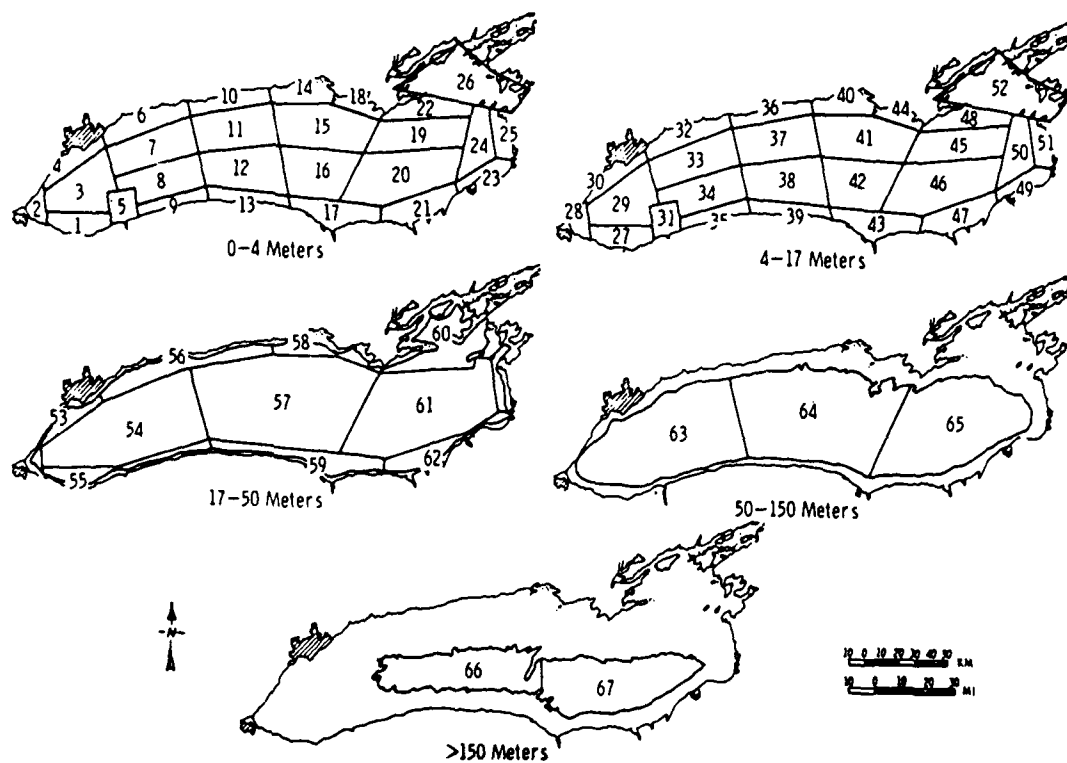


Figure 5. Lake 3 segmentation (from Thomann et al. 1975)

PART III: WATER QUALITY MODELS FOR FLOWING WATER (STREAMS AND RIVERS)

Approaches

48. Water quality models for streams and rivers range from relatively simple analytical models to more sophisticated unsteady flow models. In stream and river systems, the greatest WQ gradients generally occur or are assumed to occur along the flow axis, and 1-D (longitudinal) models that employ cross-sectional averaging are usually appropriate. Although this assumption may be valid for much of a modeled stream system, it can be violated for some localized regions, such as near discharges and downstream of the confluence of two streams. Two-dimensional analytical solutions (Fischer et al. 1980, Holley and Jirka 1986) resolve the spread and dilution of effluent plumes. These mixing models also address the question of whether a pollutant has been sufficiently diluted to meet discharge standards. Selection of an appropriate mixing model can be a tedious task if one is not familiar with the various models and their assumptions. The USEPA, Athens, GA, is incorporating these models and their protocols into an expert system to facilitate their use. This expert system will lead the user through the proper model selection and use.

49. Herein a distinction is made between stream WQ models and stream mixing models. Water quality models predict changes in WQ constituents due to transport, loadings, and reactions. Stream mixing models typically predict the initial mixing, spread, and dilution (as discussed previously), and sometimes downstream transport of a pollutant loading, but omit constituent interactions and reactions. Stream mixing models treat the pollutant as conservative and are therefore not appropriate for far-field stream WQ studies. For the latter, 1-D models are used, and often instantaneous mixing of the effluent across the stream is assumed. Although this assumption contradicts reality in localized regions near discharges, it is a practical and meaningful way of addressing most stream WQ issues. There exist a variety of approaches for 1-D stream WQ models that range from steady-state analytical solutions to dynamic numerical models.

Analytical and Numerical Steady-State Models of Stream and River Water Quality

50. Analytical solutions for 1-D stream WQ models can be derived for steady-state DO and BOD with simple first-order decay and sedimentation terms. Gromiec, Loucks, and Orlob (1983) provided formulations and solutions for a number of these models. Steady-state analytical solutions have the advantage that they can be quickly applied and have minimal data requirements. Their major disadvantage is that they require substantial simplification of stream geometry and that they do not provide time-varying information that may be required to fully address many questions.

51. Computerization of steady-state, analytical models allows easy simulation of more complex systems, such as stream networks. The USGS Streeter-Phelps model (Bauer, Jennings, and Miller 1979) and the Corps of Engineers STEADY model (Martin 1986) are examples of analytical models that allow a steady-state solution for a stream network. STEADY models temperature, DO, and BOD; the USGS Streeter-Phelps model computes DO and the components of nitrogenous oxygen demand in addition to carbonaceous biochemical oxygen demand (CBOD), orthophosphate phosphorus, total and fecal coliform bacteria, and three conservative substances.

52. When assumptions that facilitate analytical solutions either become inappropriate or do not allow for enough flexibility, it becomes necessary to resort to numerical WQ models. Numerical WQ models for river and streams vary widely in the amount of detail allowed, the number and type of WQ constituents, and whether or not the model allows for time-varying conditions. The following discussion provides an overview of two 1-D, numerical, stream WQ models that are representative of other models of their type.

53. An example of an intermediate modeling approach between fully dynamic and steady-state models is found in QUAL2E (Brown and Barnwell 1985), a model developed through and maintained by the USEPA. QUAL2E is a numerical, 1-D (longitudinal) WQ model that assumes steady flows (steady-state hydraulics) but allows simulation of either steady-state or dynamic WQ (diel variations). The model allows simulation of a total of 15 WQ constituents including: DO, CBOD, temperature, algae as Chl α , organic nitrogen, ammonia nitrogen, nitrite nitrogen, nitrate nitrogen, organic phosphorus, dissolved (inorganic) phosphorus, coliforms, an arbitrary nonconservative constituent,

and three arbitrary conservative constituents. QUAL2E has been widely used and is an accepted standard, particularly for waste-load allocation studies of stream systems.

54. QUAL2E simulates a series of piece-wise nonuniform, steady-flow segments referred to as reaches. Thus, the flows throughout the system are constant with time and uniform within each reach, but the flow and hydraulic characteristics can vary from reach to reach. The model is flexible in allowing the simulation of point and nonpoint loadings, withdrawals, branching tributaries, and in-stream hydraulic structures.

55. QUAL2E is easier to use than fully dynamic models (time-varying flow and WQ) because of the steady-state hydraulic feature. Hydraulic conditions are determined by any of three methods: (a) using stage-discharge relationships for each reach; (b) solution of Manning's equation with prismatic channel geometry information given for each reach; and (c) entering hydraulic information from another external source, such as a hydraulic step calculation, e.g. HEC-2 (Hydrologic Engineering Center 1982) or stream gaging information. Time-varying flow updates can be used with the model (Hamlin and Nestler 1987) without excessive error if the changes in flow are small and introduced gradually with respect to the system travel time.

Dynamic Models of Stream and River Water Quality

56. Fully dynamic models are required where transient events are of importance and where significant flow variations occur over periods that are much less than the travel time for the reach of interest. For example, if the travel time for a particular flow is greater than its duration, then only a portion of the reach would be exposed to that flow and its associated quality at a given time. Using steady-state hydraulics, such as in QUAL2E, the flows for all reaches would have to be incremented to the new flow condition instantaneously. In a fully dynamic model, the effects of time-varying flows and quality along the reach are considered. Fully dynamic stream WQ models are time-varying, hydraulic, or hydrologic-routing models coupled with time-varying constituent transport and transformation models.

57. A number of fully dynamic, stream WQ models are in existence (Jobson 1981, 1987; Bedford, Sykes, and Libicki 1983, Hydrologic Engineering Center 1986.). A modified version of the Bedford model, referred to as

CE-QUAL-RIV1 (Bedford, Sykes, and Libicki 1982), includes features specifically for regulated streams. CE-QUAL-RIV1 has been applied by the Corps of Engineers to a variety of regulated stream environments, including tailwaters below peaking hydropower dams, stream re-regulation (Zimmerman and Dortch 1988), and run-of-the-river navigation pools.

58. The CE-QUAL-RIV1 modeling package contains two codes, RIV1H for hydraulic routing and RIV1Q for WQ routing. RIV1H, which is similar to Fread's model (1978), solves the nonlinear St. Venant equations using the four-point implicit finite difference method with a Newton-Raphson convergence for nonlinearity. The model's formulation allows simulation of dynamically coupled branched river systems with multiple hydraulic control structures, such as weirs and low head dams. Boundary conditions may be provided in terms of flows, stages, or rating curves.

59. RIV1Q is driven by output from RIV1H or any other flow-routing model. RIV1Q uses an explicit finite difference method to solve the constituent mass balance equations. A two-point, fourth-order accurate scheme (Holly and Preissman 1977) is used for the advection term. This means that the model can accurately resolve the transport of sharp WQ gradients with little numerical diffusion. This feature can be important when simulating dynamic flow and loading conditions or when tracking a spill. The model is similar to QUAL2E in that it models temperature, DO, CBOD, and nutrient kinetics. Reaeration takes into account stream reaeration, wind-driven reaeration, and reaeration through control structures.

Inputs and Mixing Zones

60. Inputs are usually classified as point source (PS) or nonpoint source (NPS). In the vicinity of a pollutant source, one usually finds higher concentration gradients than in the receiving water body. The purpose of a mixing zone analysis or model usually is to determine the flow and concentration gradients in the vicinity of PS discharges (Lam, Murthy, and Simpson 1984).

61. Mixing zone analysis for pollution PS can have two different objectives: (a) to show sufficient dilution of an effluent near its discharge point so that a specified concentration (effluent WQ standard) is not exceeded beyond specified distances from the outlet or (b) to determine the distance

required to mix an effluent nearly uniformly (e.g. $0.9 \bar{C} < C < 1.1 \bar{C}$) with a river cross section or a layer in a stratified reservoir.

62. A mixing zone model describes the location of the isopleths as a function of river and outlet channel geometry, river flow, and effluent flow conditions. The development of the model must take into consideration the hydrodynamics of the situation. For example, a side channel discharge interacts with a river flow in several ways before the two become fully mixed. Among the flow and mixing processes generally to be considered are (Stefan 1982, Stefan et al. 1984, Muellenhoff et al. 1985): (a) jet effects due to the momentum of the discharge; (b) lateral displacement of river flow by the effluent input; (c) downstream advection by the river flow; (d) transverse turbulent mixing including secondary flow in the river; (e) buoyant spreading caused by the density difference between effluent water and river water--density depends on water temperature and total solids content; (f) vertical turbulent mixing by the river due to bed shear; and (g) mixing by navigation, structures, and similar man-made effects.

63. To facilitate the analysis, it can sometimes be considered that some of the processes occur in sequence, e.g. jet mixing before buoyancy effects. Effluent models are usually subdivided into a near field and a far field (Figure 6). In the near field, the mixing and dilution are influenced hydrodynamically by effluent conditions. In the far field, the mixing is passive and imposed by the receiving water conditions. Far field models are usually 2-D and use the advection/diffusion equation in either a horizontal or vertical plane (Krishnappan and Lau 1982, 1985). If a density differential exists between the effluent and the receiving water, a density-stratified flow may develop, especially if the receiving water is an impounded river or a lake.

64. When effluent discharges are from pipes, the near field mixing analysis may require the application of jet flow models and, in the case of complex geometries, recourse to physical models. There exist specialized numerical models for the analysis of PS releases, e.g. DISPER or TADPOL (Almquist et al. 1977) for passive mixing in the far field, and various jet and plume mixing models in uniform or stratified ambients, e.g. USEPA's PDS model (Shirazi and Davis 1974) and Ditmars' (1969) submerged jet models. For a discussion of this highly specialized topic, the reader is referred to Fischer et al. (1979) and Hoiley and Jirka (1986).

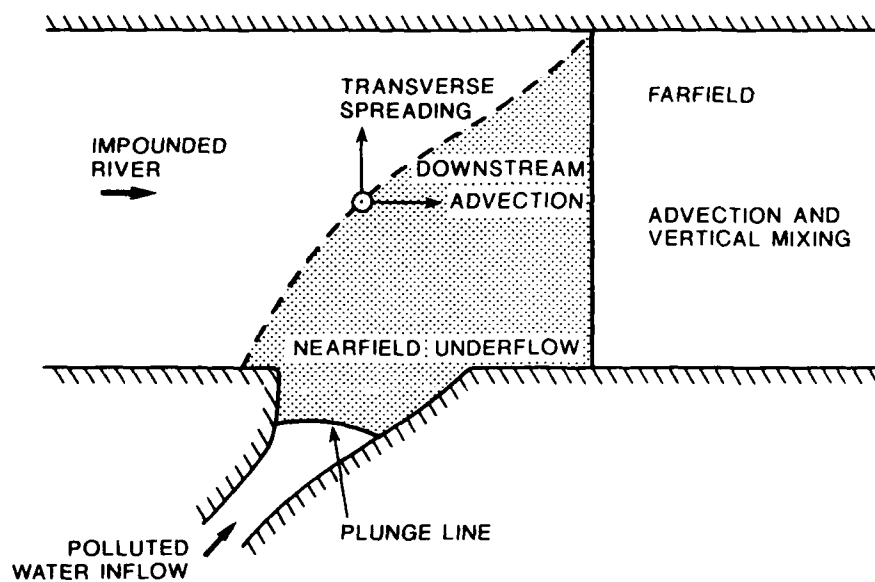


Figure 6. Near field and far field of a buoyant effluent in an impounded river

PART IV: SEDIMENT TRANSPORT AND SEDIMENT/WATER QUALITY INTERACTIONS

Concepts

65. Sediment is typically associated with agricultural runoff. Sediment not only affects water transparency, but can carry chemicals such as nutrients and toxic substances into receiving waters. Therefore, an important aspect of WQ modeling is the capability to simulate sediment transport and sediment/water interactions.

66. Aquatic sediment transport has two main forms: bed load and suspended load. Although both forms of transport can be important in streams, suspended transport is of primary interest in standing waters. Even when there is no sediment transport by the flow, sediments deposited on the bed of a stream, reservoir, or lake and not in motion can have a strong influence on WQ in the overlying water. Through adsorption, biofilm, and other chemical/biochemical transformations, stream or lake sediments can become sinks or sources of materials such as oxygen, toxic materials, or nutrients.

67. For WQ, suspended sediment and moving or stationary bed sediments are of primary interest particularly for the finer fractions of materials including silts, clays, organic detritus, and live plankton materials. Particles are characterized by size, shape, density, surface area, and surface physical and chemical properties including electric charges. Lal (1977) gives a review of particle regimes, composition, behavior, and interaction with water density.

Processes

Fall velocities, settling, deposition

68. For WQ modeling, the fall velocity of particles and their resistance to resuspension under shear stress, once they are deposited, are most significant. Fall velocities are functions of size, shape (drag coefficient), and density and can be reasonably well predicted for larger mineral particles (Dietrich 1982; Gibbs, Matthews, and Link 1971). For micron-size particles and particularly for organic particles, the large diversity in sizes, shapes, and density (Lal 1977, Ives 1973) often requires indirect determinations of fall velocities from settling traps or mass balances. Settling velocities are

used to calculate the movement of sorbed chemical downward through the water column. The deposition velocity can be estimated as the product of the settling velocity and the probability of deposition upon contact with the bed, which may range from 0 for fast, turbulent streams to 1 for stagnant pools.

Resuspension, scouring, erosion

69. Difficult also is the determination of rates of resuspension under bed shear action. For granular noncohesive materials, the relationship is "explosive" in nature. Very low or no resuspension occurs until a threshold shear stress is reached. Then resuspension rates increase proportional to some power of the excess shear stress. Powers of one have been found in estuarine studies, but powers of four and five have been found for granular river material according to a review by Akiyama and Fukushima (Wang, Shen, and Ding 1986). Rate of resuspension can be balanced by rate of deposition. At that point vertical concentration profiles above the bed show a balance of downward fluxes of sediment by settling and upward fluxes by turbulence as summarized by Vanoni (1975). According to Rouse (Vanoni 1975), the dimensionless parameter $V_s (Ku_*)^{-1}$ determines for flow over flat bottoms the degree for which vertical sediment distribution will be uniform. It will be uniform within ± 10 percent when $V_s (Ku_*)^{-1}$ is less than ~ 0.02 . V_s = particle fall velocity, $K = 0.4$, and $u_* =$ bed shear velocity $= \sqrt{\tau_b / \rho}$ with τ_b = bed shear and ρ = water density.

70. Rates of resuspension of noncohesive materials have been specified in numerous alternative forms by Ariathurai and Krone (1976); Ariathurai (1982); and Mehta (1986); Wang, Shen, and Ding (1986). Akiyama and Fukushima (Wang, Shen, and Ding 1986) specified a dimensionless resuspension rate parameter E_s as:

$$E_s = 3 \times 10^{-12} Z^{10} \left(1 - \frac{5}{Z}\right) \text{ for } 5 < Z < 13.4 \quad (11)$$

$$E_s = 0.3 \text{ for } Z > 13.4$$

where

$$Z = \frac{u_*}{V_s} R_p$$

$$R_p = (g'D)^{1/2} \frac{D}{v}$$

$g' = g(\rho_s / \rho - 1)$ = reduced acceleration of gravity of submerged particles

D = particle diameter

ν = kinematic viscosity

The resuspension (or scour or erosion) rate depends not only upon the shear stress on the benthic surface and the sediment size but also on the state of consolidation of the surficial benthic deposits. Site-specific calibration is necessary to refine initial estimates of scour.

Cohesion

71. Cohesion of particles in the deposited bed increases the resistance to resuspension and is a function of the degrees of consolidation. The investigation of this behavior by Krone, Ariathurai, Partheniades, and others have been reviewed by Mehta (1986). Besides bed shear stresses due to gravity or wind driven flows, perturbations by navigation or organisms (bioturbation) can greatly increase rates of resuspension of cohesive sediments. Effect on resuspension by wind was conceptualized by Rodney and Stefan (1987).

Coagulation and flocculation

72. Coagulation is a physical/chemical process by which particles form flocs. The flocs have higher settling velocities, and this fact affects water quality in a very significant way. This effect is used in wastewater treatment. Its significance in freshwater bodies has been studied by O'Melia (1980), among others.

Sorption

73. Suspended sediment, besides being a very important WQ parameter in its own right, can also have a very strong relationship with chemical species dissolved in the water through adsorption/desorption, e.g. of nutrients or synthetic organics (often toxic materials). This is an area of very active research (Golterman, Sly, and Thomas 1983; Stumm and Morgan 1981; Karickhoff 1984) and will be addressed in a later section in more detail.

Bottom boundary layer

74. The interaction between particles and water chemistry becomes particularly complex near the bed because of (a) strong velocity gradients in the vertical associated with shear forces; (b) activities of organisms such as biofilms, invertebrates, crustaceans, and fish; and (c) pore water movement which leaches into and out of the outlying waters. Microcosm models of these systems are necessary to provide the input or withdrawal rates of dissolved

substances. Examples are sedimentary oxygen demand (Chen, Brannon, and Gunnison 1984; Gantzer et al. 1988), phosphorous release, and PCB resuspension.

Turbidity currents

75. Sediment suspended in water can increase the density of the water/sediment mixture significantly enough so that density currents can form in "standing" waters when such mixtures are released near the shore or water surface. Particles can be deposited from such currents or eroded from the bed, and as a result, buoyancy flux is not conserved. Turbidity currents can be generated by wave action in shallow areas of lakes or reservoirs, by longshore currents, or simply by inflows; they provide a mechanism by which pollutants attached to sediment can be rapidly transported over long distances from shallow littoral waters to profundal waters. The mechanics of the erosive phase of such currents and 1-D models for their analysis exist (Akiyama and Stefan 1985) and can be incorporated in reservoir WQ models. The depositional phase of these currents is still under investigation.

Model Formulations

76. In stratified lakes and reservoirs of moderate size, advection in the horizontal direction is rapid, relative to vertical mixing, and hence only vertical gradients in SS concentration are simulated. One-dimensionality is often an acceptable assumption for smaller water bodies (of length <20 km). A relationship among SS concentration profiles, vertical turbulence, rate of deposition, and resuspension is

$$A \frac{\partial(C)}{\partial t} + \frac{\partial(V_s AC)}{\partial z} = V_s C \frac{\partial A}{\partial z} + \frac{\partial}{\partial z} \left(AK_z \frac{\partial C}{\partial z} \right) - R \frac{\partial A}{\partial z} \quad (12)$$

where C = suspended sediment concentration and V_s = fall velocity of suspended sediment in quiescent water. The first term in this equation represents the change in sediment content with time, the second term is the rate of transfer by settling from one layer to another, the third term is the rate of deposition on the sloping lake bed, the fourth term is the vertical turbulent mixing rate, and the last term is the resuspension. Vertical advection can be added to this equation.

77. There exist sediment transport models for specific purposes, e.g. modeling of alluvial channels (Dawdy and Vanoni 1986), reservoir sedimentation (Hydrologic Engineering Center 1977), estuarine water movement and sediment transport (King 1982), or simple lake turbidity (Stefan, Cardoni, and Fu 1982). Most of these models can be found referenced in recent proceedings of conferences dealing with river sedimentation (Wang, Shen, and Ding 1986), coastal engineering (Mehta 1986), reservoirs (Stefan 1981, Thomas and McAnally 1985), and lakes (Lerman 1978). Many of these models are concerned mainly with the quantity of sediment transport, locations of erosional or depositional areas, channel modification, etc. Models dealing with suspended particle transport including inorganic and organic (detritus and phytoplankton) particles and their interaction with water quality have been developed mostly for applications in eutrophication control discussed in Part V.

Examples of One-, Two-, and Three-Dimensional Sediment Transport Models

One-Dimensional Models

78. HEC-6 (Hydrologic Engineering Center 1977) computes both flow and transport. It is designed to analyze scour and deposition in rivers and reservoirs. HEC-6 and similar models are used when the flow is unidirectional and constrained to follow well-defined channels. It calculates transport of sands, silts, and clays and can handle bed-load and suspended-load transport. A 1-D turbidity model is the RESQUAL II model (Stefan, Cardoni, and Fu 1982). It computes the unsteady, vertical distribution of suspended sediment and uses it to determine light penetration for primary productivity. The attenuation coefficient η is calculated as the cumulative effect of the water, the suspended inorganic sediment (SS) concentration, and the Chl α concentration.

$$\eta = a + bSS + c \text{ Chl } \alpha \quad (13)$$

Two-dimensional models

79. Two-dimensional models include those that are integrated over depth (horizontal models) and those that are integrated over width (vertical models).

80. Horizontal 2-D modeling of sediment transport is performed by STUDH, which is part of the TABS-2 modeling system (Thomas and McAnally 1985).

STUDH is a finite element model designed for situations where the flow and transport can be satisfactorily described by depth-integrated equations. STUDH computes the bed-load or suspended-load transport of silts or clays. It obtains flows either by specification or from the TABS-2 flow model, RMA-2V. It calculates transport due either to currents alone or to currents plus short period waves (nonbreaking). The program allows for wetting and drying of cells and consolidation of fine sediments with overburden and time.

81. Laterally averaged models are applicable in studies of relatively deep narrow water bodies. Work on models of this type has been more limited than on the depth-averaged models. However, work performed during the past few years has produced a useful model, LAEMSED, produced (Johnson, Trawle, and Kee, in preparation) by adding sediment transport capability to the basic hydrodynamic/transport model LARM2 (Edinger and Buchak 1983), on which CE-QUAL-W2 is also based. A layered bed model allows for the exchange of material between the water column and the bed, but only SS transport is simulated. This model has been used to investigate the effect of navigation channel deepening on salinity intrusion and sediment transport (Johnson, Trawle, and Kee, in preparation).

Three-dimensional models

82. Two sets of three-dimensional models are in use by the WES for SS transport. They are the Resource Management Associates (RMA) series and CELC3D. Both models have a free surface, are time dependent, and allow for stratification and complex geometry.

83. The RMA series. The RMA series of programs model flow and transport in three dimensions using a finite element method. Program RMA-8 (King 1982) computes water levels and currents for constant density flows. Program RMA-10 (King 1982) computes water levels, currents, and salinity/temperature transport for flows with density gradients. SEDIMENT 8 (Ariathurai 1982) computes transport for sands, silts, or clays and contains information from Ariathurai and Krone (1976). The models permit parts of the computational mesh to be two-dimensional while employing the full three dimensions in other areas, thus ensuring economical operation.

84. CELC3D. The 3-D finite difference model of Coastal, Estuarine, and Lake Currents, CELC3D (Sheng 1983), simulates hydrodynamics and transport for temperature, salinity, and sediment. Special features include (a) a "mode-splitting" procedure which allows efficient computation of the vertical flow

structures (internal mode); (b) an efficient alternating direction implicit (ADI) scheme for the computation of the vertically integrated variables (external mode); (c) an implicit scheme for the vertical diffusion terms; (d) a vertically and horizontally stretched coordinate system; and (e) a turbulence parameterization. CELC3D provides for the resuspension, transport, and deposition of sediments where sediment particle dynamics are modeled by a consideration of particle groups and coagulation processes. Detailed dynamics within a turbulent boundary layer, under pure wave or wave-current interaction, is evaluated by means of a turbulence submodel.

85. Other 3-D models of estuaries and coastal seas were developed by Leendertse (1970, Leendertse and Liu (1975), and Onishi and Trent (1982).

PART V: MODELS ADDRESSING ORGANIC WASTES AND NUTRIENTS

Concepts

86. Water quality problems created by organic waste and nutrients include depletion of DO and stimulation of nuisance aquatic growth. In addition, high levels of nitrate or ammonia can be harmful to aquatic life.

87. Organic waste is generated by farm operations and may be carried to ponds and streams by runoff. Nutrients such as nitrogen and phosphorus are applied to fields as fertilizer and can reach surface waters by runoff and leaching. Nitrogen is more soluble and is easily mobilized by runoff or leachate water. Phosphorus is more strongly bound to soil, but may be carried by erosion. The organic matter and nutrients contained in agricultural runoff can play an important role in the trophic state and WQ of receiving waters. This section is a brief overview of the processes for modeling these constituents (referred to as conventional pollutants) and their interactions. For more detailed information, the reader should refer to other sources (Chapra and Reckhow 1983, Orlob 1983, Bowie et al. 1985, Thomann and Mueller 1987). The focus of models of conventional pollutants can be DO and BOD as a general measure of the health of the system, or it can be primary productivity when eutrophication is the major concern. These models usually include temperature, major nutrients, other chemical characteristics, detritus, bacteria, and primary producers. Water quality models for surface waters may include higher trophic levels (i.e. zooplankton and fish) because of their effect on other more important variables, such as phytoplankton, BOD, and DO. Zooplankton and fish also provide a means of controlling lower trophic levels, which can impact nutrients and DO (biomanipulation). Because the source of agricultural organic waste and nutrients is driven by the hydrologic cycle, the most appropriate modeling approaches are dynamic. For steadier leaching or irrigation situations, however, steady-state or quasidynamic models may be adequate.

Fate Processes

88. Upon entry to the surface water body, settling of particulate organic waste and nutrients generally occurs. High flow events may lead to scouring of previously deposited material. Organic matter is oxidized,

drawing upon the DO supply, which is replenished by reaeration. Organic nitrogen is mineralized to ammonia, which reaches ionic equilibrium with ammonium. Nitrification further draws upon the DO supply converting ammonia to nitrite and then nitrate. Nitrate may be converted back to ammonia or to nitrogen gas through denitrification in low DO regions of the water or sediment. Ammonia and nitrate may be taken up by phytoplankton and aquatic plants and incorporated into the food chain, eventually returning to the water as organic nitrogen.

89. Organic phosphorus is mineralized to orthophosphate, which comes to sorptive equilibrium with suspended or benthic sediment. Particulate sorbed phosphate settles; dissolved phosphate is rapidly taken up by phytoplankton and aquatic plants and incorporated into the food chain, eventually returning to the water as organic phosphorus.

90. Organic material deposited to benthic sediment is oxidized in the upper aerobic layer and reduced in the lower anaerobic layers. Upward fluxes of ammonia and reduced organic species are produced, the latter contributing to sediment oxygen demand. Particulate phosphorus may be resolubilized and may reenter the water. In some aquatic environments, net sedimentation buries a good fraction of the nutrients and organic matter deposited to the bed.

91. Although many of these interacting fate pathways are well known and included in most recent conventional WQ models, accurate simulations remain difficult. Extensive site-specific data collection is required to characterize both the sources and the rates under a range of expected conditions. Many of the rates are biologically mediated, with descriptive constants and parameters that vary both with environmental conditions and predominant species. The major pathways and cycles will be briefly discussed from the model developer's perspective.

Phytoplankton kinetics

92. Phytoplankton kinetics assume a central role in eutrophication affecting the nitrogen and phosphorous cycles, the DO balance, and food chain response. The reaction term for phytoplankton is expressed as the difference between the growth rate and the death and settling rates in a volume element. The growth rate of a phytoplankton is a complicated function of the species present and their differing reactions to solar radiation, temperature, and the balance between nutrient availability and phytoplankton requirements. Available information does not allow specification of growth kinetics for

individual species in a natural environment. Hence, models either simulate the phytoplankton community as a whole or as classes such as greens, diatoms, blue-greens, and dinoflagellates.

93. The growth rate G is usually formulated as the product of the maximum 20° C growth rate (under optimum light and nutrient conditions) with a temperature adjustment factor, a light adjustment factor, and a nutrient limitation factor.

$$G = G_{\max} X_T X_L X_N \quad (14)$$

94. Temperature is an important WQ variable because of its effect on transformation and reaction rates and aquatic life. Temperatures are calculated as described in the section on 1-D temperature stratified reservoir models. The temperature adjustment factor is usually given as

$$X_T = \theta^{T-20^\circ} \quad (15)$$

where θ is a species-specific coefficient.

95. Light attenuation functions X_L generally follow the analysis by Steele (1962, 1965), accounting for the effects of supersaturating light intensities and light attenuation through the water column, and lead to

$$X_L = \frac{2.718}{\eta d} \left\{ \exp \left[- \frac{I_o}{I_s} \exp \left(- K_e D \right) \right] - \exp \left(- \frac{I_o}{I_s} \right) \right\} \quad (16)$$

where

η = light extinction coefficient (including self shading), m^{-1}

d = depth, m

I_o = incident light intensity just below the surface, ly/day

I_s = saturating light intensity of phytoplankton, ly/day

This expression is either integrated over the day or multiplied by the fraction daylight. Generally I_s is used as a calibration parameter. Smith (1980) developed a framework for calculating I_s based upon the maximum growth rate, the quantum yield of chlorophyll, the extinction coefficient per unit of chlorophyll, and the ratio of carbon to chlorophyll in the

phytoplankton. This framework allows for adaptation by changing the carbon to chlorophyll ratio. Recent developments in phytoplankton kinetics models use photosynthetically active radiation (PAR) in $\mu\text{E m}^{-2}\text{day}^{-1}$ instead of total energy I_s (la day^{-1}). They also apply Haldane kinetics in place of Steele's equation (Megard, Tonkyn, and Senft 1984).

96. The nutrient limitation factor is based on the assumption that phytoplankton follow Monod kinetics with respect to the important nutrients. Generally, the minimum function for inorganic nitrogen and phosphorus is used:

$$X_N = \text{Min} \left(\frac{C_{IN}}{K_{MN} + C_{IN}}, \frac{C_{IP}}{K_{MP} + C_{IP}} \right) \quad (17)$$

where

C_{IN} = inorganic nitrogen, $\mu\text{g}/\ell$

K_{MN} = Michaelis half-saturation constant for nitrogen, $\mu\text{g}/\ell$

C_{IP} = inorganic phosphorus, $\mu\text{g}/\ell$

K_{MP} = Michaelis half-saturation constant for phosphorus, $\mu\text{g}/\ell$

Occasionally, X_N is expressed as the product of the nitrogen and phosphorous terms.

97. Phytoplankton "death" rates are conventionally expressed as the sum of the endogenous respiration rate, the death rate, and the grazing rate. The first two are generally modeled as a first-order temperature corrected rates. Grazing may be expressed as first order, or second order if the herbivorous zooplankton population is specified or simulated. To capture the phytoplankton population dynamics properly, zooplankton may have to be simulated. If average phytoplankton levels are adequate, then the first-order approach is acceptable.

98. Phytoplankton kinetics affect the nitrogen, phosphorus, and carbon cycles primarily through uptake and secondarily through death. Proper specification of average stoichiometry is necessary to accurately model these interactions. The ratios of phytoplankton carbon to phytoplankton nitrogen, phosphorus, and chl α vary among species and in time. Few applied-modeling frameworks account for the dynamics of stoichiometry. The user is forced to specify average values or those characteristic of stressed systems.

The phosphorous cycle

99. Organic phosphorus in the water is present in various particulate and dissolved forms that mineralize and settle at different rates. Some models lump all organic phosphorus into a single-state variable, while others divide organic phosphorus into two-, three-, or four-state variables that differ in settling and mineralization rates. Mineralization or bacterial decomposition is generally modeled as first-order temperature-corrected reaction, although second-order and saturating rates based upon phytoplankton biomass have been employed.

100. Dissolved inorganic phosphorus sorbs to suspended-particulate matter in the water column, coming to an equilibrium expressed either with a partition coefficient or as a calibrated fraction dissolved:

$$f_{DIP} = \frac{1}{1 + K_{PIP}SS} \quad (18)$$

where

f_{DIP} = fraction inorganic phosphorus dissolved,

K_{PIP} = partition coefficient, ℓ/kg

SS = suspended sediment concentration, kg/ℓ

Subsequent settling of the solids and sorbed phosphorus can provide a significant loss mechanism of phosphorus from the water column to the benthos.

Process-based functions that accurately calculate the phosphorous partition coefficient would improve prediction of this important variable significantly.

101. Dissolved inorganic phosphorus is taken up by phytoplankton at the stoichiometrically modified growth rate. While there is evidence for "luxury storage" of inorganic phosphorus in phytoplankton, most models assume only one internal pool of phosphorus as biomass. Grazing causes transfer of phytoplankton phosphorus up the food chain. Upon respiration and death, biomass phosphorus is recycled to the various forms of organic and inorganic phosphorus at user-specified ratios.

The nitrogen cycle

102. Organic nitrogen in the water is present as various particulate and dissolved forms that mineralize and settle at different rates. As for organic phosphorus, some models lump all organic nitrogen into a single-state variable, while others divide organic nitrogen into two-, three-, or

four-state variables. Mineralization to ammonia can be represented as first order or can include second-order or saturating dependence on phytoplankton biomass.

103. Ammonia nitrogen in the presence of nitrifying bacteria and oxygen is converted to nitrite, then nitrate nitrogen. The process of nitrification in natural water is complex, depending upon DO, pH, total inorganic carbon, alkalinity, Nitrosomonas and Nitrobacter bacteria, and flow conditions. Most models represent the reaction with a first-order, temperature-corrected rate constant. Some allow spatial variations calibrated by the user, or empirical DO limitations terms. Obviously, a process-based predictive function for this rate would be quite valuable.

104. Denitrification is the reduction of nitrate to ammonia and nitrogen gas. Primarily a benthic reaction, it is included in some models as a loss rate of nitrate. It is modeled as a first-order reaction, sometimes multiplied by a modified Michaelis-Menten term to suppress the reaction in the presence of a small amount of oxygen.

105. Both ammonia and nitrate are taken up by phytoplankton at the stoichiometrically modified growth rate. Some models include a preference function that calculates mostly ammonia uptake when its concentration is high enough. Grazing causes transfer of phytoplankton nitrogen up the food chain. Upon respiration and death, biomass nitrogen is recycled to the various forms of organic nitrogen and ammonia at user-specified ratios.

The carbon-dissolved oxygen balance

106. Organic carbon is present in water in various particulate and dissolved forms that oxidize and settle at different rates. Some models lump all organic carbon into a single-state variable expressed in units of oxygen--carbonaceous biochemical oxygen demand, CBOD. Other models represent various fractions of organic carbon, with their separate oxidation and settling rates. Oxidation is generally modeled as first-order temperature-corrected rate. Some allow spatial variations calibrated by the user.

107. Traditional models of organic waste do not compute inorganic carbon and the associated variables of pH and alkalinity. This carbonate system could be important for simulating the effects of acidic wastes on unionized ammonia concentrations or potential carbon dioxide limitation in low-alkalinity, high-nutrient waters. Models that include the carbonate system calculate total inorganic carbon as the sum of bicarbonate, carbonate, and

carbon dioxide. These species are in equilibrium controlled by the equilibrium constants of the dissociation reactions and the pH of the water. Carbon dioxide (and thus total inorganic carbon) is produced by respiration, consumed by algal growth, and replenished by atmospheric exchange. Carbonate alkalinity is the sum of bicarbonate concentration, two times the carbonate concentration, and the hydroxide concentration minus the hydrogen ion concentration. Addition of acids and nitrification lowers the pH and reduces alkalinity. Nitrate uptake by phytoplankton produces hydroxide and increases alkalinity.

108. Dissolved oxygen is depleted by oxidation of organic carbon, nitrification, and respiration. Benthic reactions depleting oxygen are usually modeled as a spatially variable flux of sediment oxygen demand. Respiration effects may be combined for simplicity or separated into components such as respiration by bacteria, plankton, macrophytes, fish, etc. The respiration of decomposers that utilize organic matter is referred to as decomposition. Oxygen is used during some chemical transformations, such as nitrification and the oxidation of reduced substances (e.g. sulfide, methane, reduced iron, and reduced manganese).

109. Biochemical oxygen demand (BOD) is a measure of the oxidizable matter due to biochemical processes. The problem with BOD is that it combines the effects of several oxygen-consuming processes into one variable; this approach may be too simple for modeling some systems. The more realistic approach is to separate oxygen demands into various components, such as biodegradable organic (carbonaceous) demands, nitrogenous demands, and oxidation of other substances (e.g. reduced metals, sulfide, etc.). Biodegradable organic demands may be due to dissolved and particulate matter in the water column and bottom sediments. Some models separate water column organic matter into particulate and organic matter (POM) and dissolved organic matter (DOM). Because some forms of organic matter decay at faster rates than others, organic matter may be further divided into those that decay at a fast rate (labile) and those that decay at a slower rate (refractory). As labile organic matter decomposes, a portion is transferred to the refractory state. A similar approach can be used for organic sediments. Sources of organic matter include external waste loads and excretion and mortality of living substances.

110. Dissolved oxygen is replenished by phytoplankton growth (photosynthesis) and by reaeration. Many reaeration formulas exist for streams and rivers. Those based solely on velocity and depth include O'Connor-Dobbins (for slower, deeper rivers), Churchill (for moderately deep, faster streams), and Ownes et al. (for shallow streams) (see Thomann and Mueller 1987). The Tsioglou method calculates reaeration in rivers and streams from the slope and travel time. Relationships that include the effects of bed roughness, secondary flow, and wind are under development. Numerous relationships exist for wind-induced reaeration in lakes and reservoirs. There remains a need for critical review and assimilation of all the formulas. Reaeration at hydraulic structures can be very significant.

Benthic-water interactions

111. The decomposition of organic material in benthic sediment can significantly affect the concentrations of oxygen and nutrients in the overlying waters. Aereal fluxes from the sediment due to diagenetic reactions can be substantial nutrient sources or oxygen sinks. The occurrence of anoxia may dramatically increase nutrient fluxes.

112. Most traditional models described these benthic fluxes as spatially variable source and sink terms. Some recent models have included benthic compartments where state variables are simulated. Particulate nitrogen, phosphorus, and carbon are added to the bed by settling and are lost by scour or sedimentation (burial). Dissolved species of nitrogen, phosphorus, carbon, and oxygen exchange with overlying water by pore water diffusion. Benthic oxidation rates are generally assumed first-order, with low rate constants producing ammonia and consuming organic carbon and oxygen equivalents (functionally, reduced organic species that are oxidized at the water interface). Recently, efforts have been made to simulate the diagenetic reactions and resulting fluxes more realistically (DiToro 1986). These efforts hold great promise for more accurate and predictive modeling of organic and nutrient wastes.

Simulation Models

113. Numerous simulation models of organic waste and nutrients have been developed and applied to various water bodies. Of these, only a few have been maintained for general application. To be useful for general

agricultural nutrient and organic waste simulations, a model should allow for unsteady transport and loading, phytoplankton kinetics, nitrogen and phosphorous cycles, and carbon-dissolved oxygen balances. Furthermore, written documentation and a user's manual must be available with the software.

114. Five modeling frameworks meet these criteria: WASP4-(EUTRO4), CE-QUAL-R1, CE-QUAL-W2, CE-QUAL-RIV1, and HSPF. QUAL2E may be useful for steady-loading situations. Such models as DEM, EXPLORE, RECEIVII, WRECEV, MINLAKE, and AUTO-QD meet these criteria but are not actively maintained and supported by a central, public distribution center. Different versions of these and others may be maintained privately by consultants and local Government agencies and may be useful for those water bodies where setup and calibration have previously been accomplished.

115. Stream Quality Model QUAL2E (Brown and Barnwell 1985) is a steady-state model for conventional pollutants in 1-D streams and well-mixed lakes. The conventional pollutants include conservative substances, temperature, bacteria, BOD, DO, nitrogen, phosphorus, and algae. QUAL2E is widely used for waste-load allocations and discharge permit determinations in the United States and other countries. WASP is designed to permit easy substitution of user-written routines into the program structure. Problems that have been studied using WASP include BOD, DO dynamic, nutrients and eutrophication, bacterial contamination, and toxic chemical movement.

116. Eutrophication WASP (EUTRO4) (Ambrose et al. 1988) combines a kinetic structure adapted from the Potomac Eutrophication Model with the WASP transport structure. EUTRO4 predicts DO, CBOD, phytoplankton, carbon, and chl *a*, ammonia, nitrate, organic nitrogen, and orthophosphate in the bed and overlying waters.

117. WASP4 is linked to DYNHYD4 (Ambrose et al. 1988), a simple link-node hydrodynamic model capable of handling variable tidal cycles, wind, and unsteady inflows. It produces an output file that can be linked with WASP4 to supply the flows and volumes to the WQ model.

118. Hydrological Simulation Program FORTRAN (HSPF) (Johanson et al. 1984) is a comprehensive package for simulation of watershed hydrology and WQ for both conventional and toxic organic pollutants. HSPF incorporates the watershed-scale Agricultural Runoff Model (ARM) and NPS models into a basin-scale analysis framework that includes pollutant transport and transformation in stream channels.

119. The model uses information such as the time history of rainfall, temperature, and solar radiation; land-surface characteristics such as land-use patterns and soil properties; and land-management practices to simulate the processes that occur in a watershed. The result of this simulation is a time history of the quantity and quality of runoff from an urban or agricultural watershed. Flow rate, sediment load, and nutrient and pesticide concentrations are predicted. The program takes these results, along with information about the stream network and PS discharges, and simulates instream processes to produce a time history of water quantity and quality at any point in a watershed--the inflow to a lake, for example. HSPF includes an internal data base management system to process the large amounts of simulation input and output. The models CE-QUAL-R1, CE-QUAL-W2, and CE-QUAL-RIV1 were discussed in previous sections.

PART VI: SYNTHETIC ORGANIC CHEMICALS

Fate Processes

Ionization

120. Ionization is the dissociation of a chemical into multiple-charged species. Consider a weak acid AH_3 or base BH_3 :



These reactions are rapid. At equilibrium, the distribution of chemicals between the unionized and the ionized species is controlled by the pH of the water and the ionization constants.

121. Stronger acids and bases may undergo further ionization, controlled by ionization constants K_{a2} , K_{a3} , K_{b2} , and K_{b3} . Ionization can be important because of the different toxicological and chemical properties of the unionized and ionized species.

Sorption

122. Sorption is the bonding of dissolved chemicals onto solid phases S_i , such as benthic and suspended sediment, biological material, and sometime dissolved or colloidal organic material.



These reactions are usually fast relative to other environmental processes, and equilibrium may be assumed. For environmentally relevant concentrations (less than $10^{-5}M$ or one-half water solubility), equilibrium sorption is linear with dissolved chemical concentration (Karickhoff 1984) or:

$$C_i = K_{pi} \times C_d \quad (22)$$

where

C_i = chemical concentration in phase i, mg/kg

K_{pi} = the sorption partition coefficient for phase i, ℓ/kg of phase i

C_d = dissolved chemical concentration, mg/ ℓ

At equilibrium, then, the distribution among the phases is controlled by the partition coefficients K_{pi} . The total mass of chemical in each phase is controlled by K_{pi} and the amount of solid phase present.

123. Values for the partition coefficients can be obtained from laboratory experiments. For organic chemicals, lab studies have shown that the partition coefficient is related to the hydrophobicity of the chemical and the organic matter content of the sediment. Normalization of the partition coefficient by the organic-carbon content of the sediment has been shown to yield a coefficient, K_{OC} , that is relatively independent of other sediment characteristics or geographic origin. Correlation of K_{OC} with the water solubility of the chemical or the octanol/water partition coefficient of the chemical has yielded successful predictive tools for incorporating the hydrophobicity of the chemical in an estimate of its partitioning. These correlations do poorly for chemicals with very low or very high hydrophobicity, however, because of deviations from hydrophobic adsorption. Chemicals containing polar functional groups and low octanol/water partition coefficients tend to exhibit hydrophilic contributions to adsorption, whereas large nonpolar molecules with high octanol/water partition coefficients generally require long periods to reach equilibrium resulting in low estimates of K_{OC} when sorption is measured over short time frames. The latter effect is particularly significant because it suggests that the assumption of instantaneous equilibrium used by the toxic chemical models may not be valid for those chemicals for which adsorption is the most important process.

124. In addition to the assumption of instantaneous equilibrium, implicit in the use of Equation 22 is the assumption of reversibility. Laboratory data for very hydrophobic chemicals suggest, however, that a hysteresis exists, with desorption being a much slower process than adsorption. Karickhoff (1984) suggests that this effect may be the result of intraparticle kinetics in which the chemical is slowly incorporated into components of the sorbent. This phenomenon is not well understood. A quantitative modeling framework to characterize it was proposed by Di Toro (1985).

125. Sorption can be important in controlling both the environmental fate and the toxicity of chemicals. Sorption may cause the chemical to accumulate in bed sediments or bioconcentrate in fish. Sorption may retard such reactions as volatilization and base hydrolysis or may enhance other reactions including photolysis and acid-catalyzed hydrolysis.

Settling, deposition, and scour

126. Suspended particles carrying sorbed chemicals can settle through the water column and deposit on the underlying bed. Benthic particles carrying sorbed chemicals can scour and become suspended in the water column. Mass fluxes for settling, deposition, and resuspension are controlled by the settling, deposition, and scour velocities, and the concentrations of suspended and benthic sediment.

Loss kinetics

127. Chemical concentrations and resulting observed toxic effects often decline downstream due to physical and chemical reactions. For constant environmental conditions, the overall chemical loss rate is often approximated as a first-order reaction:

$$m_k = -K_T \times C \times V \quad (23)$$

where

K_T = observed loss coefficient, in days⁻¹

C = total chemical concentration, g/m³

V = volume of water plus sediment, m³

The observed loss coefficient K_T represents a single set of environmental conditions only. Changes in temperature, velocity, depth, sunlight, wind, sediment concentration, or pH can affect the total loss rate in unknown ways.

128. A method to complement field survey data is the chemical process approach. This approach combines laboratory-measured chemical constants with field-measured environmental properties to estimate site-specific rate coefficients, $K_i(x,t)$, for several loss processes "i";

$$K_i(x,t) = K_i \times E_i(x,t) \quad (24)$$

where K_i is a laboratory-measured second-order rate constant and $E_i(x,t)$ is the intensity of the relevant environment parameter. If more than one loss process is active for a chemical in an environment, the overall loss coefficient can be estimated by summing the individual rate constants. Combining the chemical process approach with the field survey approach should increase the reliability of modeling estimates, allowing extrapolation to a much wider range of environmental conditions.

129. The loss processes considered in most chemical fate models include volatilization, hydrolysis, photolysis, and bacterial degradation. Chemical oxidation and reduction are sometimes included as well.

130. Volatilization is the flux of a chemical across the air-water interface. Its rate is proportional to the gradient between the dissolved concentration in the overlying atmosphere. For most chemicals, the partial pressure in the atmosphere is negligible and the equation reduces to a first-order form with the removal rate coefficient, K_v , expressed:

$$K_v = -k_v \times f_d \times d^{-1} \quad (25)$$

where

k_v = conductivity of the chemical, m/s

f_d = fraction of the chemical concentration that is dissolved

d = average water depth, m

131. The conductivity is influenced by both chemical properties (molecular weight, Henry's Law constant) and environmental conditions at the air-water interface (turbulence-controlled by wind speed, current velocity, and water depth). Toxic chemical models either require the user to input a value for k_v or internally compute a value using the two-film theory first proposed by Lewis and Whitman (1924). This theory assumes that the rate of transfer is controlled by diffusion through laminar layers in the air and water at the interface in which the concentration gradients driving transfer are localized.

132. The liquid and gas transfer coefficients are dependent on turbulence at the interface, on temperature, and on properties of the chemical such as diffusivity. Empirical correlations have been developed relating transfer coefficients either directly to physical parameters such as wind velocity and the density and viscosity of the water (Southworth et al. 1979a; MacKay and Yeun 1983), plus the molecular weight and diffusivity of the chemical or to the field-measured transfer coefficients of oxygen and water vapor (Liss and Slater 1974). O'Connor (1983) has presented a theoretical development of the liquid transfer coefficient applicable to a wide range of hydrodynamic conditions, but application requires estimates of several coefficients and wind data that are not easily obtained.

133. Hydrolysis is a reaction in which cleavage of a molecular bond of the chemical and the formation of a new bond with either the hydrogen or the hydroxyl component of a water molecule occurs. Hydrolytic reactions are usually catalyzed by acid and/or base, and the overriding factor affecting hydrolysis rates at a given temperature is generally hydrogen or hydroxide concentration (Wolfe 1980). The overall hydrolysis rate constant in most toxic chemical models is calculated by:

$$K_H = \Sigma(k_{HAi} \times [H^+] + k_{HNI} + k_{HBI} \times [OH^-]) \quad (26)$$

where

- k_{HAi} = acid hydrolysis rate constant for phase i, L/mole-s
- $[H^+]$ = hydrogen ion concentration, moles/L
- k_{HNI} = neutral hydrolysis rate constant for phase i, s⁻¹
- k_{HBI} = alkaline hydrolysis rate constant for phase i, L/mole-s
- $[OH^-]$ = hydroxide ion concentration, moles/L

The models do not compute hydrogen or hydroxide ion concentrations. Instead these are input to the models assuming that their concentrations are unaffected by the hydrolysis reaction because of the low concentration of the toxic chemical present and reacting.

134. Photodegradation (photolysis) is the transformation or degradation of a compound that results directly from the adsorption of light energy. It is a function of the quantity and wavelength distribution of incident light, the light adsorption characteristics of the compound, and the efficiency at which absorbed light produces a chemical reaction. Photolysis is classified into two types that are defined by the mechanism of energy absorption. Direct photolysis is the result of direct absorption of photons by the toxic chemical molecule. Indirect or sensitized photolysis is the result of energy transfer to the toxic chemical from some other molecule that has absorbed the radiation.

135. A quantitative framework that permits the prediction of direct photolysis from the incident light and the characteristics of the chemical (Zepp and Cline 1978) has been incorporated in several of the toxic chemical modeling frameworks. Use of this framework in natural water systems is complicated by the lack of a satisfactory model of ultraviolet-light penetration that incorporates the effects of both dissolved organics and particulate

material in the water. A comprehensive framework for photolysis also must include sensitized photolysis. Unfortunately, the spectrum of compounds, particularly dissolved organics, involved in photochemical reactions is not known (Miller 1983). In addition, valid frameworks to predict free radical reactions have not been developed, and the importance of these reactions remain undetermined (Zepp 1980).

136. A less rigorous method for predicting a photolysis rate coefficient K_p involved extrapolations of observed rates from one environmental condition to another:

$$K_p = K_{PG} \times (L) \times \sum \phi P_i \times f_i \quad (27)$$

where

K_{PG} = observed rate coefficient in s^{-1} for a reference light intensity

$[L]$ = fraction of the reference light intensity averaged through water column

ϕP_i = relative yield for the chemical in phase i

f_i = fraction of the total chemical concentration in phase i

The reference light fraction $[L]$ accounts for depth, light extinction, cloud cover, latitude changes, and surface light variability.

137. Biodegradation encompasses the broad and complex process of enzymatic attack by organisms on organic chemicals. Bacteria, and to a lesser extent fungi, are the mediators of biological degradation in surface water systems. Dehalogenation, dealkylation, hydrolysis, oxidation, reduction, ring cleavage, and condensation reactions are all known to occur either metabolically or via cometabolism. Cometabolism refers to degradation of chemicals by microorganisms that are not capable of utilizing the chemical as a substrate for growth. Biodegradation is generally assumed to follow Michaelis-Menten enzyme kinetics. Values for the half-saturation constant K_m and the maximum rate of degradation are not easily measured. Toxic chemical models generally assume that the chemical concentration is much less than the half-saturation constant and simplify the Michaelis-Menten equation to:

$$K_B = -B_{\max} \times K_m^{-1} \times B = -k_B \times B \quad (28)$$

where K_B is the second-order rate coefficient in millilitres per cells per day. The bacterial activity, B in cells per millilitres, is fundamentally the

concentration of the enzyme reacting with the toxic chemical. Enzyme concentration cannot be measured in the field; however, the environmental and ecological effects on its activity are difficult to estimate (Lewis et al. 1984).

138. The growth kinetics of the bacterial population degrading a toxic chemical are not well understood. The presence of competing substrates and of other bacteria, the toxicity of the chemical to the degrading bacteria, and the possibilities of adaptation to the chemical or cometabolism make quantification of changes in the population difficult. As a result, toxic chemical models assume a constant biological activity rather than modeling the bacteria directly. Often, measured first-order biodegradation rate constants from other aquatic systems are used directly.

Simulation Models

139. Numerous simulation models have been developed for toxic chemicals in surface water systems. Of these, only a handful have been developed for general application. To be useful for general agricultural chemical simulations, a model must include benthic and water column compartments, unsteady transport and loading, partitioning and transformation reactions. Furthermore, written documentation and a user's manual must be available along with the software.

140. Seven modeling frameworks described here meet these criteria: EXAMS (Burns et al. 1982, Burns and Cline 1985), a quasi-dynamic model for organics; WASP (DiToro et al. 1983; Ambrose et al. 1983, 1986, 1988; Connolly and Winfield 1984) and HSPF (Johanson et al. 1984), dynamic compartment models for organics and metals; SERATRA (Onishi and Wise 1982), FETRA and TODAM, 1- and 2-D dynamic models for organics and metals; and UTM-TOX (Browman 1983), a dynamic multimedia model for organics and metals. These frameworks differ mainly in the degree of specificity incorporated in the transport, transfer, and reaction processes, the allowable spatial and temporal resolution of the problem, and the manner in which sediment is defined.

141. Exposure Analysis Modeling System (EXAMS-II) is both a steady-state and a quasi-dynamic model designed for rapid evaluation of the behavior of synthetic organic chemicals in aquatic ecosystems, including lakes, rivers, and estuaries. EXAMS-II is an interactive program that allows the user to specify and store the properties of chemicals and ecosystems, modify the

characteristics of either via simple Englishlike commands, and conduct rapid, efficient evaluations of the probable fate of chemicals. EXAMS-II simulates a toxic chemical and its transformation products using second-order kinetics for all significant organic chemical reactions. EXAMS-II does not simulate the solids with which the chemical interacts. The concentration of solids must be user-specified for each compartment. The model accounts for sorbed chemical transport based on solids concentrations and specified transport fields. Benthic exchange includes pore water advection, pore water diffusion, and solids mixing. The latter describes a net steady-state exchange associated with solids that is proportional to pore water diffusion. EXAMS is supported by USEPA's Center for Exposure Assessment Modeling, Athens, GA.

142. Water Quality Analysis Simulation Program (WASP4) (Ambrose 1988) is a generalized modeling framework for contaminant fate in surface waters including lakes, rivers, and estuaries. Based on the flexible compartment modeling approach, WASP4 can be applied to 1-, 2-, or 3-D given transport between segments. WASP4 can read output files from the link-node hydrodynamic model DYNHYD4, which predicts unsteady flow rates in unstratified rivers and estuaries given variable tides, wind, and inflow. A variety of WQ problems can be addressed with the selection of appropriate kinetic subroutines. Two general toxic chemical modeling frameworks have been constructed from WASP-TOXIWASP (Ambrose et al. 1983) and WASTOX (Connolly and Winfield 1984, Connolly and Thomann 1984). These separate frameworks are combined in WASP4. The WASP models are supported by USEPA's Center for Exposure Assessment Modeling, Athens, GA.

143. The TOXI4, subset of WASP4, simulates up to three interacting toxic chemicals and up to three sediment size fractions in the bed and overlying waters. First- or second-order kinetics can be used for all significant organic chemical reactions. Benthic exchange includes pore water advection, pore water diffusion, and deposition/scour. Net sedimentation and burial rates can be specified or calculated. An empirically based food chain model is linked to TOXI4 for calculating chemical concentrations in biota and fish resulting from predicted aquatic concentrations.

144. Hydrological Simulation Program FORTRAN (HSPF) is a comprehensive package for simulation of watershed hydrology and WQ for both conventional and toxic organic pollutants. The HSPF simulates three sediment types (sand, silt, and clay) in addition to specific organic chemicals and transformation

products of those chemicals. The reaction and transfer processes included are hydrolysis, oxidation, photolysis, biodegradation, volatilization, and sorption. Sorption is modeled as a first-order kinetic process in which the user must specify a desorption rate and equilibrium partition coefficient for each of the three solids types. Resuspension and settling of silts and clays (cohesive solids) are defined in terms of shear stress at the sediment-water interface. For sands, the capacity of the system to transport sand at a particular flow is calculated, and resuspension or settling is defined by the difference between the sand in suspension and the calculated capacity. Calibration of the model requires data for each of the three solids types. Benthic exchange is modeled as sorption/desorption and deposition/scour with surficial benthic sediments. Underlying sediment and pore water are not modeled. The HSPF is supported by USEPA's Center for Exposure Assessment Modeling, Athens, GA.

145. The Sediment Radionuclide Transport Model (SERATRA) framework (Onishi and Wise 1982) is a time-variable model for simulating radionuclides or organic chemicals in river systems. It solves the 2-D (vertical and longitudinal) advection-dispersion equation using finite element techniques for one chemical and three types of solids (sand, silt, and clay). Scour and deposition of solids are defined in identical fashion to that in HSPF. The transfer and reaction processes included are hydrolysis, photolysis, oxidation, biodegradation, volatilization, and sorption. Volatilization is computed from a user-specified oxygen transfer coefficient, limiting consideration of volatile organics to those that are liquid-film controlled. Sorption is modeled as a first-order kinetic process for each of the three solids types. Benthic exchange is modeled as sorption/desorption and deposition/scour with surficial benthic sediments. Underlying sediment and pore water are not modeled. A similar 1-D (longitudinal) version for rivers (TODAM) and a 2-D (longitudinal and lateral) version for estuaries (FETRA) are also available from Batelle Pacific Northwest Laboratories, Richland, WA.

146. The Unified Transport Model for Toxicants (UTM-TOX) (Browman et al. 1983) is an upgrade of the Unified Transport Model (UTM) originally developed to model heavy metal ions. It is a time-variable framework that includes atmospheric, terrestrial, and aquatic components. The aquatic component is designed to simulate streams and rivers. The transfer and reaction processes include sorption, volatilization, hydrolysis,

biodegradation, and first-order photolysis. Sorption is described by an equilibrium partition coefficient. Sorbed phases are assumed unreactive (1982 version). UTM-TOX is available from Oak Ridge National Laboratories, Oak Ridge, TN.

PART VII: METALS

147. Metals are found naturally in the Earth's crust. As a result of irrigation in some regions, metals may be solubilized and transported to surface waters. Steady or quasi-dynamic modeling approaches should be adequate if irrigation practices do not change.

Fate Processes

148. Upon entry to the surface water body, metal speciation may change because of complexation, precipitation, sorption, and redox reactions. Metals concentrations are further diluted by additional streamflow and mixing. Physical loss can be caused by settling and sedimentation, whereas a physical gain may be caused by resuspension.

Metal complexation, precipitation

149. Heavy metals can form complexes with organic and inorganic liquids and precipitate or dissolve:



where

M^+ = metal ion

L_1 and L_2 = liquids (such as carbonate, sulfide, or humate)

ML_1 = soluble complex

K_{ri} = equilibrium coefficient for reaction 1

ML_2 = insoluble complex

K_{spi} = solubility product for reaction 1

Reaction times range from essentially instantaneous to thousands of years. At equilibrium, the distribution of metals among the possible complexes is controlled by the amount of metal and liquids present and the reaction coefficients and solubility products. In natural waters, sorption also affects the distribution by reducing the amount of metal available for complexation and precipitation.

150. Complexation reactions can affect transport by either increasing or decreasing the soluble fraction. Sometimes one chemical species is known to be much more toxic than another for a given heavy metal. This is especially important because some states and USEPA have been moving towards "site-specific water quality standards," in which chemical speciation will be considered on a site-by-site basis. For example, a site that is known to have a great deal of naturally occurring dissolved organics may not require as stringent a WQ standard because the dissolved organic material may complex the heavy metal and render it nontoxic to biota.

Sorption

151. Heavy metals frequently absorb or "bind" to solid surfaces. The mechanism of sorption or attachment is via: (a) physical absorption to solid surfaces, (b) chemical sorption or binding by liquids at the solid water interface, or (c) ion exchange with an ion at the solid water interface. In addition, if the heavy metal is complexed in solution by an organic liquid, it could sorb into the organic solid phase much like an organic pollutant. The mathematical formulation for describing the partitioning of the heavy metal between the solid phase and the aqueous phase is the same as for organic chemicals except the K_{pi} is usually called the "distribution coefficient" for heavy metals (although it may be referred to as the partition coefficient or the binding constant in some cases). In most measurements and simulation models, all soluble complexes are lumped with the free ion to give the dissolved metal concentration. Precipitated metal is lumped with all sorbed species to give total particulate metal concentration. A spatially variable lumped-distribution coefficient K_D describes the two phases. There is no general consistency in reported K_D values for particular methods in the natural environment, so site-specific values should be used when possible.

Redox reactions

152. Metals can change oxidation states through various oxidation and reduction reactions:



where

M^{++} = oxidized metal

e^{-} = an electron

M^+ = reduced metal

K_{ri} = equilibrium coefficient for reaction i

Under some conditions, the kinetics of oxidation or reduction may be important to simulate.

Simulation Models

153. Two kinds of simulation models have been developed for metals in surface water systems. One addresses aquatic transport and fate, while the other addresses metals chemistry. The former are those general toxic chemical models that include benthic and water column compartments, partitioning, and particulate settling, resuspension, and sedimentation. These include MICH Riv, a steady-state model for organics and metals; TOXI WASP, WASTOX, WASP3, WASP4, and HSPF, dynamic compartment models for organics and metals; SERATRA, FETRA, and TODAM, 1- and 2-D models for organics and metals; and UTM-TOX, a dynamic multimedia model for organics and metals. All of these have been discussed in an earlier section.

154. The second kind of simulation model addresses metals chemistry. Those developed for general application include organic and inorganic complexation, sorption, precipitation and dissolution, and redox reactions. These models are single compartment equilibrium models that calculate speciation for specified environmental conditions based on a set of thermodynamic constants. Environmental conditions, such as metal concentrations, liquid concentrations, pH, pE, and temperature, must be specified by the user. Thermodynamic constants are usually included in a data base with the model. Examples of these models include MINTEQ (Felmy 1984) and MINTEQA1 (Brown and Shiao 1981); REDEQL and MINEQL; WATEQ (versions 1-4); and GEOCHEM.

155. Proper application of these models requires some specialized expertise because kinetic limitations at particular sites may prevent the thermodynamically possible reactions. Nevertheless, thoughtful application may reasonably describe the predominant metals species at a site and thus give useful insight into potential migration patterns and biological effects. For agricultural leaching problems, these models must be run in conjunction with one of the transport and transformation models described above.

156. MINTEQA1 (Felmy et al. 1984, Brown et al. 1987) is a geochemical model that is capable of calculating equilibrium aqueous speciation,

absorption, gas phase partitioning, solid phase saturation states, and precipitation-dissolution of 11 metals (arsenic, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc). MINTEQA1 contains an extensive thermodynamic data set and six different algorithms for calculating absorption. MINTEQA1 is supported by USEPA's Center for Exposure Assessment Modeling in Athens, GA.

PART VIII: CHALLENGES AND RECOMMENDATIONS

157. Several challenges in the state of the art of WQ modeling are apparent.

158. The composition of WQ models introduces and combines uncertainties from several sources. A recent review by Beck (1987) examines (a) model structure, (b) model parameters, (c) propagation of prediction errors, and (d) experimental design to reduce critical uncertainties. In practical applications of WQ models, uncertainty in input data is often a major limitation. In Beck's assessment, there is ample evidence that "larger," more "comprehensive" models are easily capable of generating highly uncertain prediction of future behavior. Figure 7 gives the frame of reference for the analysis of uncertainty (Beck 1987). Aspects of model uncertainty are also addressed in stochastic modeling (see Reckhow and Chapra 1983). Model sensitivity to parameter variability and confidence levels of model outputs from probabilistic distributions of inputs are sometimes generated. Progress in this area will raise the reliability of models and help to identify "optimum sophistication in water quality modeling."

159. Current WQ concerns are with numerous toxic substances such as heavy metals, e.g. mercury, lead, cadmium, and chlorinated organics (e.g. DDT, PCB, Dieldrin, etc.). The pathways and ultimate fates of these substances through ecosystems are often not fully understood, and thus, limit the formulation of useful and reliable forecasting models at this time (Dolan and Bierman 1982, Thomann and DiToro 1983). There is a need to improve understanding and descriptions for processes affecting contaminant transport and fate, such as partitioning of contaminants to solids and bacterial decomposition. Additionally, work should focus on the transport of surface water contaminants to ground water. The verification of contaminant models has been greatly limited by the expense of collecting appropriate data. Therefore, confidence in these models will remain limited until proper verifications are performed. As a tool to assess research needs, the models are, however, very useful at this stage. Among the uncertainties are adsorption/desorption processes, interactions of organics and sediments, and surface chemistry. The formulation of adsorption isotherms frequently (Sweeney et al. 1982) pose problems in model formulation. The problem applies to suspended sediments as well as deposited (bottom) sediments.

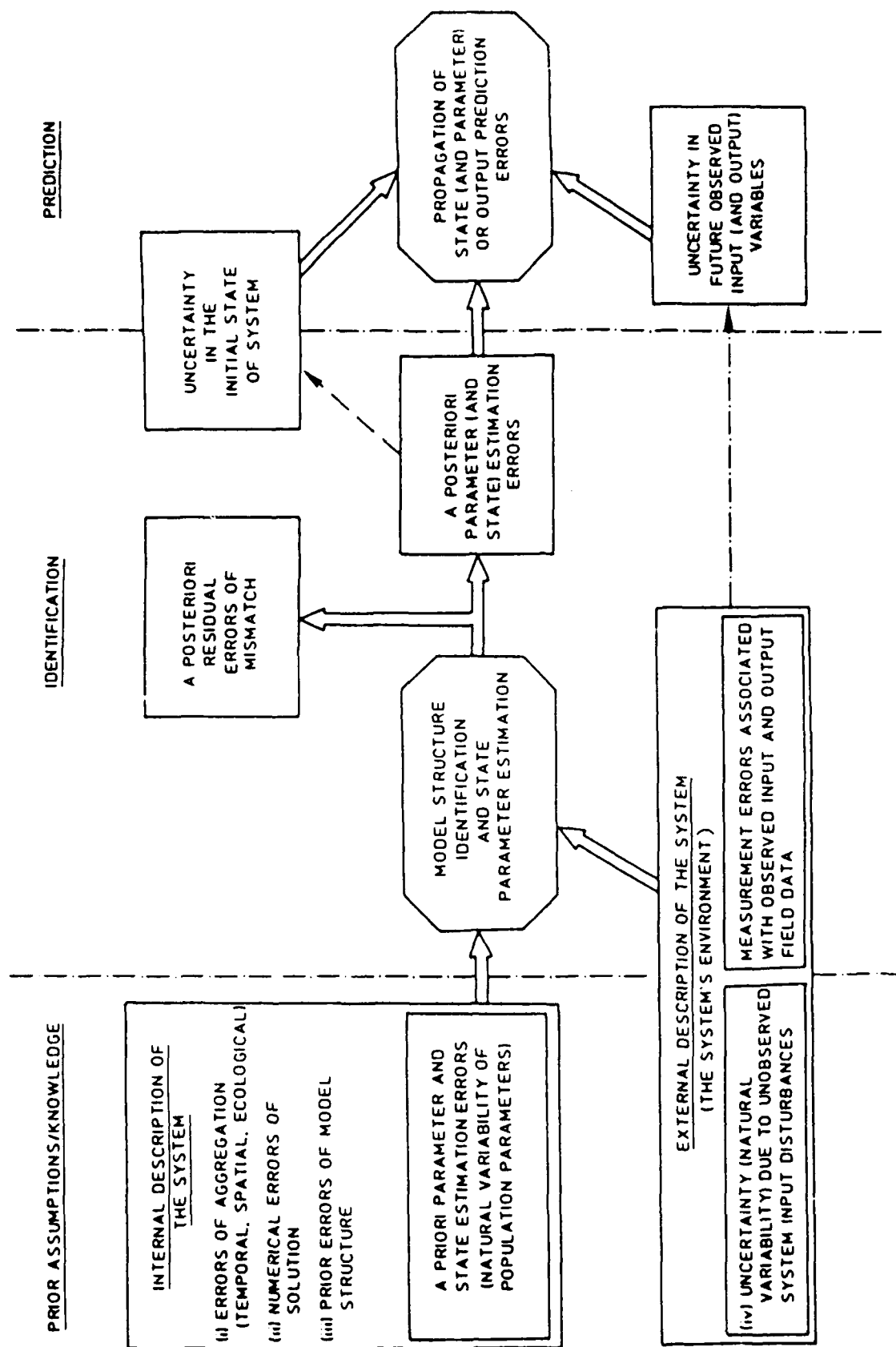


Figure 7. Frame of reference for the analysis of uncertainty (from Beck 1987)

160. Models which quantify the role of pH in aquatic ecosystems have been formulated (Schnoor et al. 1987; Lang 1987; Weater, Bishop, and Beck 1986) and are being refined with the intent to assist in the selection of appropriate acid rain abatement strategies. While basic chemical relationships to pH are known, the biological response can often not be quantified yet.

161. The greatest need in the area of conventional (DO/nutrient) WQ modeling is the development of reliable models that predict sediment diagenesis and fluxes from and to the bottom sediments. Water quality models will not be truly predictive until the bottom sediments are interactively coupled with the water column to provide time-varying SOD and nutrient fluxes that are predictable from previous conditions. Although some work has been started in this area (Hatcher 1986), there is still much study necessary. Proper sediment modeling will require an accounting of labile and refractory forms of particulate and dissolved organic matter in both the water column and bottom sediments.

162. Capabilities for "number crunching" by supercomputers continue to rise dramatically. This appears to permit recourse to replace some empirical relationships with more fundamental ones, e.g. in flow simulation or in chemical partitioning. It is likely that in the long term most of the benefits will come from the ability to simulate long time frames in multidimensions with the hydrodynamic and WQ model run on the same temporal and spatial scales. The biological parameters will probably continue to require numerous empirical relationships.

163. Spin-offs of artificial intelligence technology have resulted in computerization of knowledge-based and expert systems. Development of these systems for WQ models will improve user/computer interfaces and greatly reduce the difficulty of selecting and applying these models. Other related aspects are the development of preprocessors and postprocessors, graphics, and other decision support.

164. Although complexity of some WQ models makes their application for daily decision making impractical, managers should understand what are available and now they can be used. The USEPA through its WQ modeling program and other agencies and universities can provide modeling packages and assistance. Some models are compact enough to be used on personal computers (PC's) and micros. User-friendly programs developed for PC's permit decision-makers to

manipulate data bases and to screen management options. This can be useful during managerial planning and policy discussions (Chapra and Canale 1987, Canale and Auer 1987).

165. Remote sensing offers intriguing possibilities for synoptic investigation of large areas, e.g. of reservoirs. It appears that multispectral scanner information can be correlated with some WQ parameters collected onsite (ground truth). If these correlations can be strengthened in further research, remotely sensed spatial distributions of surface WQ can be compared with model simulations. This can be useful for model verification and also for updating of initial conditions for model simulations. The combination of remote sensing with WQ models may offer a reasonably inexpensive means to follow WQ evolutions in real time, e.g. for reservoir management.

Table 1
Some Typical WQ Models

<u>Parameters</u>	<u>All Water Bodies</u>	<u>Pond, Lake, Reservoir</u>	<u>River</u>	<u>Estuary</u>
Agricultural pollutants				
Sediment or total suspended solids	WASP4	CE-QUAL-R1 CE-QUAL-W2 RESQUAL II	HSPF SERATRA TODAM	CE-QUAL-W2 FETRA SED-III
Organic waste and nutrients	WASP4- (EUTRO4)	CE-QUAL-R1 CE-QUAL-W2 MINLAKE	QUAL2E CE-QUAL-RIV1 HSPF	CE-QUAL-W2
Synthetic organics	EXAM-II WASP4- (TOXI4)		HSPF SERATRA TODAM UTM-TOX	FETRA
Metals transport	WASP4- (TOXI4)		MICHRIV HSPF SERATRA TODAM UTM-TOX	FETRA
Metals speciation	MINTEQA1 MINEQL WATEQ3 GEOCHEM			

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